THERMODYNAMIC INVESTIGATIONS UPON CARBENIUM IONS DERIVED FROM PYRIDYLDIPHENYLMETHANOLS--FREE AND COMPLEXED

By

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This is dedicated to the Spirit of Bombastus, for he was blessed with the courage and the desire to seek the Philosopher's Stone. In so doing he was magnificently rewarded, for instead he found the truth.

This is also dedicated to my Mother and to one Suffering Bastard from Iowa. For without their inspiration this work would not have been completed.

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THERMODYNAMIC INVESTIGATIONS UPON CARBENIUM IONS DERIVED FROM PYRIDYLDIPHENYLMETHANOLS - FREE AND COMPLEXED

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Major Department: Chemistry

The syntheses of a series of 2- and 4-pyridyl-R-phenyl-4-fluorophenylmethanols are reported; R may be 4-H, 4-CH_3, or 4-OCH_3, within each series of alcohols. Palladium(II) complexes of the 4-pyridyl alcohols have been prepared also wherein either a single alcohol is included in the coordination sphere of the metal to yield the so called "mono"-alcohol complexes, or two identical alcohols are included to yield the so called "bis"-alcohol complexes. The corresponding 2-pyridyl alcohol complexes could not be prepared presumably as a result of steric difficulties. These trityl-type alcohols (and their complexes) are precursors to stable arylcarbenium ions obtained via dissolution in $HClO_4$-H_2O, the ionizing medium.

The "Deno" H_R acidity function titration technique, ^{19}F nmr chemical shift measurements, and free energy parameter correlation analyses, have afforded a quantitative evaluation of the stabilities of the various carbenium ion species. These investigations have also

furnished information which elucidates the stabilizing effect contributed by the coordinated metal containing moiety to a given complexed carbenium ion.

Two particularly noteworthy outgrowths have resulted from these studies. First, internally consistent electronic spectral interpretations have been obtained which indicate that the stabilizing influence exerted by the metal center on a given complexed carbenium ion is reflected by the frequency changes of the carbenium ion absorption bands detectable upon coordination of the ion. Secondly, appropriate, linearly interdependent free energy correlations have given rise to the development of arguments which indicate that although complexation (for the cases considered herein) stabilizes a carbenium ion relative to the corresponding protonated ion, coordination does in fact destabilize a pyridylcarbenium ion relative to the unprotonated free ion species.

INTRODUCTION

The Carbonium Ion

The imperspicuous nature of the term "carbonium ion" stems from the fact that this nomenclature classification has been applied to all types of multivalent carbocations throughout the chemical literature. This problem has been pointed out by McManus and Pittman (1) and more recently by Olah (2). These authors have stated that the term "carbenium ion" is a more systematic reference towards trivalent carbocations (i.e., R_3C^+) which contain a sextet of valence electrons. This follows in that these trivalent carbocations are valence isoelectronic with such ions as oxenium and sulfenium. Here the suffix "-enium" distinguishes these ions from their "-onium" counterparts. Furthermore, this nomenclature directly establishes a relationship to the species which results from carbene ($:CH_2$) protonation, namely the carbenium ion (CH_3^+). Therefore throughout this work the term carbenium ion shall be employed as an explicit reference to a trivalent carbocation with a valence electron sextet. Specifically the cations considered herein are those which are derived from pyridyldiphenylmethanols upon dissolution of these alcohols in suitable, strongly acidic media.

Preliminary Considerations

The preparation of various bis(pyridyl)phenylcarbinols and tris-(pyridyl)carbinols has been reported by J. P. Wibaut et al. (3). These workers recognized the direct structural and electronic similarity of these pyridinecarbinols to triphenylcarbinol (triphenylmethanol) and therefore investigated their halochromic properties in 100% sulfuric acid solution. They discovered however, that such solutions exhibited no color whatsoever. Thus, these pyridinecarbinols were not ionized in strong acid in a fashion akin to that of triphenylcarbinol. That is there was little, if any, conversion of the pyridinecarbinols to the corresponding trityl-type carbenium ion.

None the less this disclosure provoked further speculation as to whether or not such tertiary aromatic alcohols could be converted to the corresponding carbenium ion. Indeed it seemed to be the case that the principal difference in the behavior of these pyridine alcohols, as compared with their benzene homologues, was attributable to the degree of positive charge development which would supervene upon their dissolution in strongly acidic media. Thus, the concentration of positive charge produced through base site protonation (of the pyridine ring nitrogen atoms) would be sufficient to prevent carbenium ion formation owing to the concomitant development of like charge repulsions. Therefore it seemed reasonable that if these basic sites could be chemically bound in order to prevent protonation upon treatment with strong acid, it would then be feasible to generate the carbenium ion.

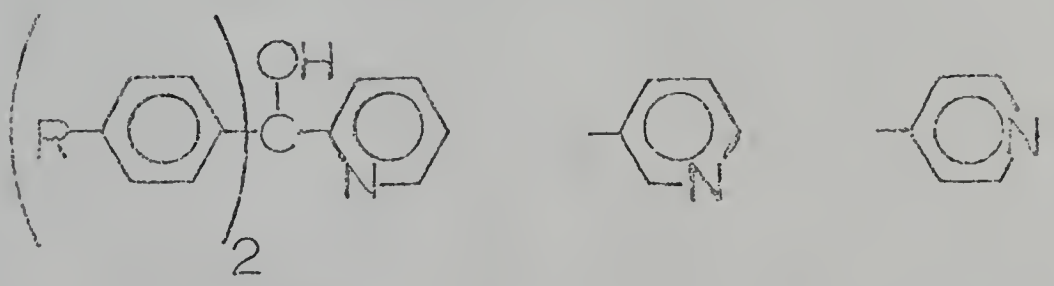
Moreover, it was recognized that such investigations upon mono-pyridyldiphenylcarbinols were very much relevant to this consideration.

That is, it was expected that this type of simpler pyridine alcohol could be converted to a reasonably stable carbenium ion since this transformation would be accompanied by the development of less positive charge. This possibility was substantiated through the work of Smith and Holley (4) wherein they reported that two structural isomers of monopyridyldiphenylmethanol were measurably ionized in concentrated sulfuric acid solution. Thus, it appeared that carbenium ions derived from these particular monobasic alcohols could be employed for stability investigations upon such ionic species as they are produced in suitable acidic media; and with respect to the possibility of inhibiting pyridine nitrogen protonation upon carbenium ion generation, the binding of these basic nitrogens through coordinate bond formation to an essentially neutral metal center seemed to be an appropriate method of general applicability. Therefore investigations upon carbenium ions stabilized by this attendant limitation of positive charge build-up would be permitted. Also, since pyridine is a ligand which is known to exhibit π-acid behavior (5:117), the potential for measuring the enhancement of ion stability as a consequence of coordinated atom (ion) "back-donation" was established. That is, if the species bound to the pyridine nitrogen possessed occupied valence orbitals of appropriate symmetry and energy to interact with the π-system of the carbenium ion by creating π-character in the metal-nitrogen bond, the ion could also be so stabilized. Thus, if the coordinate bond(s) was sufficiently stable as to remain intact upon conversion of such complex compounds to the corresponding carbenium ion(s), these considerations would be experimentally accessible. (The consequences of σ- and π-bonding interactions between a coordinated carbenium ion and a prospective metal center have been

discussed rather elegantly by Richardson (6:10-11) and are here referred to conveniently.)

Groundwork to this Research

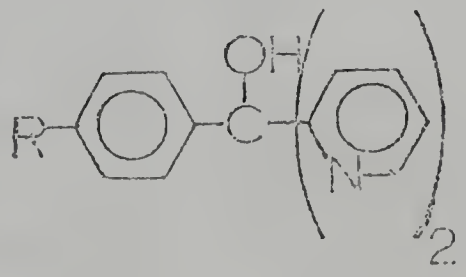
In 1966 Bhattacharyya and Stoufer (7) began work in this area of research. In accord with standard synthetic methods they prepared various monopyridyldiphenylmethanols (Figure 1) as well as bis(2-pyridyl)-phenylmethanols (Figure 2). Preliminary investigations upon the free alcohols revealed, as expected, that the monopyridyl derivatives were converted to the corresponding trityl-type carbenium ion upon treatment



(2-pyridyl) (3-pyridyl) (4-pyridyl)

R = -H, $-CH_3$, $-OCH_3$, $-N(CH_3)_2$

Fig. 1. Monopyridyldiphenylmethanols (pyLOH)



R = -H, $-CH_3$, $-OCH_3$, $-N(CH_3)_2$

Fig. 2. Bis(2-pyridyl)phenylmethanols (py_2LOH)

with reagent sulfuric acid (96% H_2SO_4). The bis(pyridyl)alcohols, however, were not ionized by this solvent to any appreciable degree. This agreed with the results of Wibaut et al. (3). Much of the initial work was therefore directed towards the utilization of the monopyridylalcohols both as carbenium ion precursors and as heteroaromatic donor species. In conjunction with this, Bhattacharyya and Stoufer successfully prepared a number of palladium(II) complexes of these monopyridylalcohols by employing them as neutral donor ligands. The materials obtained were well-characterized as the neutral dichlorobis(alcohol) complexes of palladium(II). These complexes were of the general formula $Pd(II)(pyLOH)_2Cl_2$, where pyLOH represents the "ionizable" pyridine alcohol. These compounds were diamagnetic and square planar as expected for 4-coordinate complexes of palladium(II). (See, for instance, the discussion concerning the complexes of palladium(II) by Hartley (5:17-19).)

Subsequent investigations by these workers upon the carbenium ions derived from these palladium complexes revealed that dilution of the ionizing medium (i.e., the 96% H_2SO_4 solution) with water afforded the reisolation of the intact neutral complex. This experimental find indicated that the pyridine-metal coordinate bond was reasonably stable in strongly acidic media. In this way a tangible basis for examining the stabilities of such coordinated carbenium ions was established.

The results of Bhattacharyya and Stoufer served to demonstrate that the monopyridyldiphenylmethanols were suitable σ-donor ligands as well as carbenium ion precursors. To continue with this work, Richardson (6) prepared a series of palladium(II) complexes of the bis-(2-pyridyl)phenylmethanols which had been synthesized previously by Bhattacharyya and Stoufer. These complexes were of the general formula

$Pd(II)(py_2LOH)Cl_2$, and were presumably 4-coordinate about the metal center with the alcohol functioning as a bidentate ligand. It had been anticipated that as a consequence of binding the nitrogen donor sites through coordination to the metal that these compounds could be converted to the complexed carbenium ion(s). It was discovered, however, that by employing customary experimental methods this ionization was not achievable. There was no obvious explanation to account for this result. Perhaps it was the case that the dissolution of these complexes in strong acid was accompanied by simultaneous rupture of the metal-nitrogen coordinate bonds. Since there exists a considerable degree of steric strain in these 2-pyridyl complexes as a consequence of spatial crowding between the metal center and the carbinol carbon, this coordinate bond rupture upon acid treatment was not unlikely.

Richardson carried on with investigations on the stability of carbenium ions derived from the 4-pyridyldiphenylmethanols. He recorded the electronic spectrum of the free alcohols and of their palladium(II) complexes in neat trifluoroacetic acid (TFA). These solutions were highly colored thereby indicating carbenium ion formation with TFA as solvent. The visible region of the spectrum of these colored solutions revealed the presence of two intense, broad absorption bands which were shown to be characteristic of the carbenium ions. An examination of the visible spectrum of triphenylmethylcarbenium ion produced by dissolving triphenylmethanol in trifluoroacetic acid showed the same strong absorption bands. Indeed when the electronic spectrum of solutions of these materials in nonionizing media (e.g., methanol or glacial acetic acid) was examined in the visible region, these strong absorption bands were found to be absent. It was also observed during

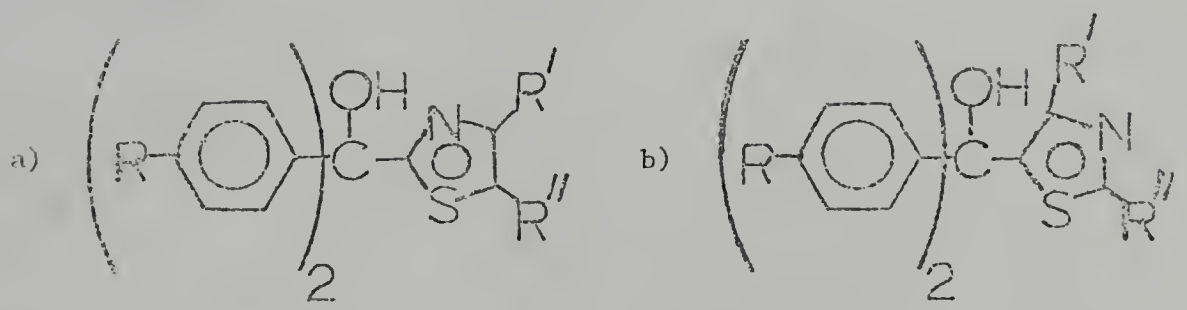
these spectral examinations that the positions of these absorption bands for a given carbenium ion species shifted upon going from the uncomplexed protonated carbenium ion to the corresponding metal-complexed carbenium ion. This suggested that there was a direct relationship between the stability of the carbenium ion and the attendant alteration in electronic environment associated with pyridine nitrogen protonation vs. pyridine nitrogen coordination.

Similar band position shifts were also detectable as the para-substituent (R) on the phenyl rings in the alcohols was varied within the series R = -H, to R = $-CH_3$, to R = $-OCH_3$. In this instance the band shifts were attributed to resonance electronic interactions between the R-substituent and the carbenium ion center. It was also found that the stability of the ion was considerably increased when R = $-OCH_3$. This reflected a substantial capacity of para-OCH_3 to participate in favorable conjugational interaction with the π-system of the trityl-type ion.

Richardson ultimately attempted to establish a relationship between carbenium ion development in these 4-pyridyldiphenylmethanol systems and measurable proton (^1H) nuclear magnetic resonance (nmr) chemical shifts. To do this the ^1H nmr spectra of TFA solutions of these alcohols and their palladium(II) complexes were recorded. Then to fingerprint the phenyl proton and pyridyl proton absorptions the TFA solution spectra were compared with the solution spectra of the unionized compounds. Also to facilitate the resolution and identification of the various proton signals, these nmr spectra were subjected to computer simulated analyses. These investigations however, proved to be unsuccessful

in that the proton absorptions of the unionized compounds could not be correlated unambiguously with the proton absorptions of the corresponding carbenium ions.

As a logical extension of the work upon the pyridylmethanols Wentz (8) prepared a series of structurally related alcohols by substituting a thiazole ring for the pyridine ring. These materials were 2-, and 5-thiazolyldiphenylmethanols (Figure 3). The similarity of these alcohols to the pyridyl alcohols is apparent. In accord with previous work the neutral palladium(II) bis-complexes of these alcohols were prepared. These compounds were of the general formula $Pd(II)(ThOH)_2X_2$, with X representing a coordinated halide ion, either chloride (principally) or bromide. Wentz had considered that the replacement of



R = -H, $-CH_3$, $-OCH_3$; R' = -H, $-CH_3$; R'' = -H, $-CH_3$

a) 2-Thiazolyldiphenylmethanol (2-ThOH); b) 5-Thiazolyldiphenylmethanol (5-ThOH)

Fig. 3. Thiazolyldiphenylmethanols

pyridine with thiazole would add a degree of uniqueness to the anticipated chemical behavior of such heterocyclic bases. That is, since the pyridine and thiazole heterorings are isoelectronic and contain essentially identical nitrogen atoms they should exhibit like donor characteristics. However, because thiazole also contains a thiophene type sulfur atom, the thiazole-substituted alcohols should be precursors to carbenium ions with somewhat different stability than those got from the analogous pyridine alcohols. Turnbo and coworkers (9) had indeed demonstrated that the thienyl moiety could enhance the stability of such carbenium ions relative to the corresponding phenyl-substituted carbenium ion. They did this by determining the equilibrium constants (K_{eq}) for the reaction

$$R^{+} + 2\,H_2O \rightleftarrows R\text{-}OH + H_3O^{+} \qquad \{1\}$$

in reagent sulfuric acid for a series of structurally equivalent thienyl and phenyl carbinols. The K_{eq} values were experimentally measured by employing the spectrophotometric method of Deno and coworkers (10). An ordering of the equilibrium data which were obtained revealed that a given thienyl-substituted carbenium ion is more stable than the related phenyl carbenium ion. Thus, these data also established that the sulfur atom in the thienyl nucleus was not protonated by the sulfuric acid as this development of additional positive charge would have induced a net destabilization of these thienyl carbenium ions. Thus, it was reasonable to expect that the thiazolyldiphenylmethanols would be sources of triaryl carbenium ions more stable than those which were got from the pyridyldiphenylmethanols. Furthermore,

the ionization of the thiazolyl alcohols could be investigated by the same techniques used for studying the thienyl ions since the pyridine alcohols had been shown to be ionizable in concentrated sulfuric acid. In fact the stability of the thiazolyl ions could be quantitatively evaluated provided the acid solvent ionized the parent alcohols to an extent of one hundred percent (100%). In other words, if the degree of conversion of alcohol to carbenium ions was measurable in terms of the capacity of the acid solvent to produce ionization as a function of acid concentration, then any equilibrium pertinent to alcohol-ion interconversion would presumably be monitorable. Undoubtedly it had been with criteria such as these in mind, that Deno and coworkers (10) were able to define an acidity function regarding the ionization of arylmethanols in concentrated sulfuric acid – water. The results of Turnbo and coworkers (9) proved the suitability of applying Deno's "acidity function" technique towards following alcohol – carbenium ion equilibria in the thienyl systems. Therefore it seemed reasonable to employ this method for quantitative studies upon thiazolylalcohol – carbenium ion equilibria, provided the alcohols could be completely ionized at a known solvent concentration.

Wentz made a very important contribution when he demonstrated that many of the thiazolyl alcohols were converted completely to carbenium ion in reagent perchloric acid (70% $HClO_4$). This was accomplished by examining the visible absorption spectrum of these alcohols as perchloric acid solutions at various acid concentrations. This simple investigation revealed that for relatively high acid concentrations the carbenium ions derived from many of these alcohols exhibited a Beer's law dependence; but, as these acid solutions were systematically diluted by the

addition of measured increments of deionized water, this Beer's law dependence was no longer maintained. From these observations it was concluded that in the high acid concentration regions carbenium ion formation was effectually 100%, and the result of adding small quantities of water was to dilute the concentration of the absorbing species (i.e., the carbenium ion). However, as more water was added, the equilibrium described by equation {1}, (which represents the reconversion of thiazolyl carbenium ion to thiazolyl alcohol), began to be shifted significantly to the right as written. A plot of carbenium ion absorbance vs. weight percent (wt %) $HClO_4$ served to reflect these observations. This plot over a region of high acid concentrations yielded a straight line for a completely ionized thiazolyl alcohol. This was the Beer's law portion of the plot. But, at an acid concentration particular to the alcohol under investigation, a marked change in slope was observed. That is, the plot began to deviate considerably from an extrapolated Beer's law line. It was at this acidity region where the concentration of the absorbing species (the carbenium ion) was being diminished not only by being diluted, but also as a consequence of being reconverted to the nonabsorbing neutral alcohol precursor. Thus, absorbance fall off was magnified considerably as the ionizing solvent was made progressively more dilute.

Thus, by applying appropriate acidity function data (made available by Deno and coworkers (11) for aqueous perchloric acid) Wentz was able to measure spectrophotometrically equilibrium constants for the generation of carbenium ions resulting from the dissolution of free and complexed thiazolyldiphenylmethanols in reagent perchloric acid. This investigation therefore allowed a quantitative ordering of the stabilities

of carbenium ions derivable from these heterocyclic basic compounds. The trends in stability which were established by this study, and the pertinent generalizations which these trends served to warrant, are summed up accordingly:

(i) Carbenium ions derived from 5-thiazolyl alcohols are more stable than those got from the corresponding 2-thiazolyl alcohols. This illustrates the inherent destabilizing effect that charge repulsion has on carbenium ion development. Since the sites of positive charge are three bonds separated in the 5-thiazolyl ions, vs. two bonds separated in the 2-thiazolyl ions, and models of these species indicate a likely "through-space" charge interaction for the 2-thiazolyl ions, this trend in stability is certainly expected.

(ii) For a particular alcohol, R-group substitution in the para position on the phenyl rings, for the series R = -H, $-CH_3$, $-OCH_3$, results in an increase in carbenium ion stability. This reflects conjugational stabilization of positive charge development known for this particular series of "R" groups as para substituents in trityl-type carbenium ions. (See, for instance, the results reported in the papers by Taft and McKeever (12), McKinley et al. (13), and Deno and coworkers (10).)

(iii) For a particular alcohol R'-, or R"-group substitution on the thiazole ring (see Figure 3), and for R' = -H, $-CH_3$, and for R" = -H, $-CH_3$, results in an increase in carbenium ion stability as "R" is increased in mass. This exhibits the greater ability of $-CH_3$ compared with -H to inductively release electron density.

(iv) Carbenium ions derived from the palladium complexes, Pd(II)-$(ThOH)_2X_2$, are more stable than those got from the corresponding free alcohols. This, at least, illustrates the effect of binding the basic

sites in the ligands through coordinate bond formation with an essentially neutral species. This obviously minimizes positive charge development upon treatment with strong acid since ligand protonation is now prevented.

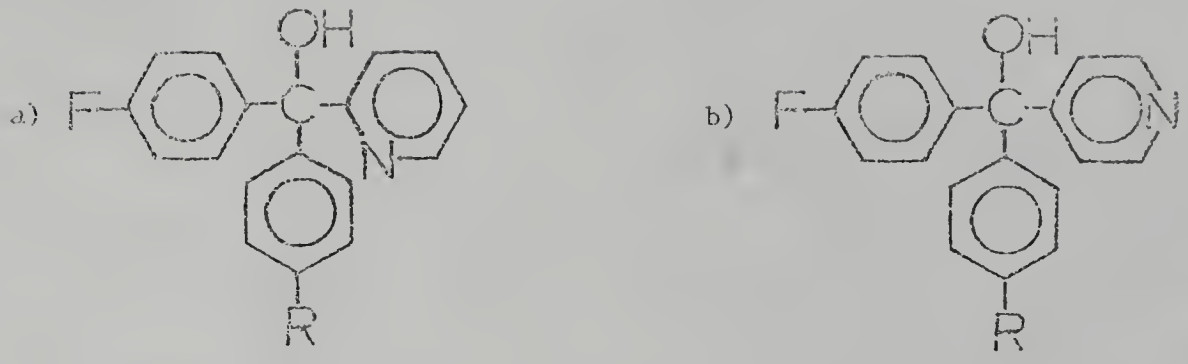
(v) In the instances investigated, carbenium ions derived from the complexes $Pd(II)(ThOH)_2Br_2$, are more stable than those got from the corresponding chloride ligand complexes. This suggests that a backbonding mechanism is operative through which the metal center donates π-electron density into empty π-orbitals of appropriate symmetry on the coordinated carbenium ion species. Thus, bromide, which is expected to be a better π-donor than chloride, should in turn contribute a net stabilizing effect on the ion <u>via</u> donation of π-electron density into suitable <u>empty metal</u> orbitals.

Two final investigations of consequence were carried out. The equilibrium constant for the conversion of triphenylmethanol to triphenylcarbenium ion in perchloric acid was measured. The value obtained was found to be in good agreement with the value which had been reported for this ionization by Deno and coworkers (11). This served further to verify the reliability of the thermodynamic data got for the generation of thiazolyl carbenium ions. And lastly, the ionization of 4-pyridyldi(p-tolyl)methanol in perchloric acid was examined. The 4-pyridyldi(p-tolyl)carbenium ion was found to be more stable than the 2-thiazolyl carbenium ions but less stable than the 5-thiazolyl carbenium ions. This result was significant in that it allowed a comparison of these heterorings to be made, as if they were position isomers, with respect to their ability to stabilize trityl-type carbenium ions. More importantly, this result demonstrated the appropriateness of the

spectrophotometric technique of Deno and coworkers (10) for studying pyridyldiphenylmethyl carbenium ions. Therefore carbenium ions derived from the pyridine alcohols previously investigated by Bhattacharyya and Stoafer (7), and by Richardson (6), could now be studied quantitatively and broaden considerably the scope of this work.

The research reported in this dissertation deals principally with investigations upon free and complexed carbenium ions derived from pyridyldiphenylmethanols. These pyridine alcohols and the complexes thereof were prepared such as to be especially suitable for thermodynamic stability studies.

The alcohols considered are specifically 2-, and 4-pyridylphenyl-4-fluorophenylmethanols (Figure 4). The 4-fluorophenyl ring has been incorporated into the molecular framework of the pyridylmethanols to provide a ^{19}F nmr probe uniquely sensitive to the development of positive charge upon carbenium ion formation. Considerations for the application of ^{19}F nmr techniques towards stability studies on these ions were prompted by the unsuccessful ^{1}H nmr investigations which, for similar purposes, had been attempted by Richardson (6). The single fluorine nucleus is particularly suitable for use as a diagnostic nmr tag in these systems. The principal reasons are the following. First, with but one such resonating nucleus in the species under investigation, the spectrum obtained is not complex and is therefore amenable to straightforward interpretation. Secondly, fluorine in the 4-position on a phenyl ring is known to be highly sensitive to changes in electron density in the π-system of the ring. See, for instance, the papers by Taft et al. (14,15), Dewar and Marchand (16), and Pews, Tsuno, and Taft



R = -H, $-CH_3$, $-OCH_3$

a) 2-Pyridylphenyl-4-fluorophenylmethanol (2-pyLOH)

b) 4-Pyridylphenyl-4-fluorophenylmethanol (4-pyLOH)

Fig. 4. Pyridylphenyl-4-fluorophenylmethanols

(17), which report that changes in π-electron density in an aromatic system may be precisely correlated with 4-fluorophenyl ^{19}F nmr chemical shifts. These results therefore indicate that the fluorine nucleus must participate in π-bonding interactions with the aromatic ring to which it is attached. Thus, ^{19}F nmr chemical shift data obtained for a "4-fluorophenyl" fluorine would reflect any changes in π-electron density throughout a conjugated system in which this phenyl ring was incorporated. And so, of primary significance is the relationship which exists between the magnitude of the fluorine chemical shift for a particular pyridyldiphenylcarbenium ion, and the thermodynamic stability of that ion. The ^{19}F nmr studies by Filler (18) and Schuster (19) and their coworkers upon tris-(p-fluorophenyl)carbenium ion in different ionizing solvents demonstrated the suitability of this experimental

consideration by independently determining K_{R^+} for this cation-carbinol equilibrium from ^{19}F chemical shift data.

This work also focuses upon the use of the Deno spectrophotometric titration technique for quantitative measurements of the stabilities of carbenium ions derived from free and complexed pyridylphenyl-4-fluorophenylmethanols. The thermodynamic data so obtained are then compared with corresponding ^{19}F nmr chemical shift data *via* correlation analysis methods. This data treatment is carried out for the purpose of establishing interdependent relationships existing between the stability information got from each of these types of physical measurement.

In keeping with previous work the neutral bis(alcohol) palladium(II) complexes, $Pd(II)(pyLOH)_2Cl_2$, were prepared and studied by the physical methods described above. However, since these materials contain two moles of "ionizable" alcohol per mole of complex, the degree of positive charge development upon carbenium ion generation is questionable. This difficulty had been encountered by Wentz (8) in his investigations upon the thiazolyl complexed carbenium ions. In an attempt to resolve this problem complexes of the type $Pd(II)(pyLOH)(L_N)Cl_2$ were prepared. In these new materials, L_N represents a neutral, nonionizable ligand which remains coordinated upon carbenium ion generation. Thermodynamic studies on these new complexes yield information which directly relates the nature of a singly charged coordinated carbenium ion to the stabilizing influence of the metal center. Thermodynamic data are presented herein which are in respect to the following equilibria:

$$H^+pyL^+ + 2\,H_2O \rightleftarrows H^+pyLOH + H_3O^+ \qquad \{2\}$$

$$Cl_2L_NPdpyL^+ + 2\ H_2O \rightleftarrows Cl_2L_NPdpyLOH + H_3O^+ \quad \{3\}$$

$$Cl_2Pd(pyL)_2^{2+} + 4\ H_2O \rightleftarrows Cl_2Pd(pyLOH)_2 + 2\ H_3O^+ \quad \{4\}$$

Equation {2} pertains to the aqueous titration of an uncoordinated pyridyldiphenylmethyl carbenium ion. This equation is written to emphasize that the pyridine ring remains protonated throughout the reconversion of carbenium ion to alcohol. This transformation is associated with a positive charge change of 2+ to 1+. Equation {3} corresponds to the titrimetric reconversion of a singly charged coordinated carbenium ion to the neutral palladium complex precursor. This process is associated with a charge change of 1+ to 0. Equation {4} is a composite statement of what actually may be at least two stepwise processes; initially (perhaps) the reconversion of a species containing two coordinated carbenium ions to a species with but one coordinated ion, followed by complete reconversion to the neutral palladium bis-alcohol complex. This process may therefore be associated with two full units of positive charge change, viz., 2+ to 0. Considerations for purposes of critically evaluating the thermodynamic data obtained from investigations upon these equilibria are accounted. The apposite conclusions which follow have been presented and are carefully discussed.

EXPERIMENTAL

Synthesis of Ligands

The pyridyldiphenylmethanols which have been employed as heteroaromatic donors (and as carbenium ion precursors) in this research, were prepared by standard Grignard synthetic methods. This generally involved the addition of an ether solution of the appropriate 2- or 4-pyridyl ketone to an ether solution of the required Grignard arylmagnesium halide, followed by acid hydrolysis of the salt-like intermediate to yield the desired alcohol. Since the necessary ketones were also made in this laboratory, the synthetic methods for their preparation have been included. A list of the special, commercially obtained reagents employed in these procedures, with names of suppliers, is provided in Table I.

The same apparatus and assembly was used in the preparation of each of the ligands (alcohols) and ketones. All glassware connections were with standard taper ground joint fittings unless otherwise specified. All glassware was scrupulously cleaned and dried prior to assembly. All ground joints were carefully lubricated by the application of a very small quantity of Dow Corning silicone grease. Rotation of the connected joints within one another assured the deposition of a uniform film of lubricant. The assembled apparatus consisted of a 3-necked,

one-liter round bottom flask equipped with a ground glass stirring shaft in the center neck. The stirring shaft was fitted with a Teflon stir paddle, and the shaft was lubricated with the minimum amount of 8117 stirrer lubricant, "Stir-Lube," Ace Glass Co., Vineland, New Jersey. Stirring speed was regulated with a rheostat controlled electric stirring motor. The side necks of the flask were fitted respectively with a 250 ml pressure equalizing addition funnel and a one-liter capacity, Dewar type condenser charged with dry ice during preparative runs. The condenser was attached to the flask with a ball joint connection which facilitated reaction vessel manipulation required to maintain controlled atmosphere conditions throughout the system. Immediately following assembly the system was purged with a steady stream of dry nitrogen gas. The nitrogen environment was maintained until the hydrolytic step was reached. All syntheses were performed using anhydrous diethyl ether as solvent. Magnesium metal turnings used for Grignard reagent preparation were conveniently activated (unless described otherwise) by placing the required quantity of turnings into the dry reaction flask and stirring them vigorously for a period of 24 — 36 hours at ambient temperature. This procedure reduced the metal to a finely divided gray-black powder which usually reacted readily with the appropriate aryl halide to yield the desired Grignard (20). Grignard formation was initiated by gentle warming of the reaction mixture. If this reaction became too vigorous, cooling the flask with a cold water bath slowed the reaction to an equable rate. The subsequent addition of reagents to the Grignard (in situ) was done at reduced temperature by cooling the reaction flask with an insulated

bath containing a mixture of chloroform and dry ice. The temperature of the bath was regulated by the addition of dry ice as needed.

4-Fluorophenyl-2-pyridylketone. Fluorophenylmagnesium bromide was prepared essentially by the method outlined by McCarty and coworkers (21). A solution of 63 ml (95 g, 0.54 mol) 4-bromofluorobenzene in 200 ml ether was added dropwise to 13 g (0.53 mol) of activated magnesium. The mixture was slowly stirred, and the reaction proceeded smoothly as evidenced by the gentle ebullition of ether and the formation of a brownish sludge. Following the complete addition of the ether — aryl halide solution the mixture was brought to gentle reflux by warming the reaction flask with a "Glas-Col" heating mantle. Grignard formation was presumed to be complete following reflux for a period of 10 - 12 hours.

The remainder of the procedure paralleled the method of de Jonge et al. (22). The fluorobenzene Grignard solution (above) was cooled to -35°. A solution of 26 g (0.25 mol) 2-cyanopyridine (picolinonitrile) in 200 ml ether was then added dropwise to the Grignard. This immediately resulted in the separation of a tan-colored solid. The reaction mixture was stirred continuously during the addition of the 2-cyanopyridine to prevent lumping of the tan solid. After all of the 2-cyanopyridine had been added the cooling bath was removed, and stirring was continued until the reaction mixture warmed to ambient temperature. The flask and contents were then cooled to -80°, and the ketimine addition compound was hydrolyzed by the careful addition of 50 ml ice water. This was followed by the addition at 0° of 100 ml concentrated HCl solution resulting in the formation of a yellow (upper) ether layer

and a red-brown (lower) aqueous — acid layer. The ether layer was drawn off and discarded, and the aqueous layer was treated carefully with concentrated NH_3 solution until a pH of 6 — 7 was obtained. This resulted in the separation of copious quantities of a yellowish precipitate. This material was washed with deionized water and then shaken with sufficient fresh ether until all the solid was redissolved. The other phase was evaporated to yield 40 g (80%) of the ketone, a light tan solid which melted at 79 — 81°. The ketone was purified by vacuum sublimation to yield a white crystalline solid melting at 83 — 84°.

4-Methylphenyl-2-pyridylketone (p-tolyl-4-pyridylketone). A hexane solution of n-butyllithium (63 ml, 1.6 M) was placed in the reaction flask and diluted with 250 ml ether. This solution was cooled to -40°, and an ice-cold solution of 10 ml (17 g, 0.11 mol) 2-bromopyridine in 100 ml ether was added dropwise with stirring. During the addition of the bromopyridine the reaction mixture became an orange slurry which changed gradually to a yellow-green slurry. Following the complete addition of the bromopyridine, stirring was continued until the reaction mixture warmed to -30°. The reaction mixture was then recooled to -45°, and a solution of 13 g (0.11 mol) p-tolunitrile (p-methylbenzonitrile) in 100 ml ether was added dropwise with stirring. This resulted in the formation of a yellow slurry. Following the addition of the nitrile stirring was continued until the reaction mixture warmed to ambient temperature. The reaction mixture was now recooled to -40° and hydrolyzed by the dropwise addition of 200 ml 2 M HCl. The ether was distilled off, and the reaction mixture was

warmed to 100° and stirred for 1 hour at this temperature to facilitate ketimine decomposition. The aqueous reaction mixture was cooled in ice and neutralized by the careful addition of 6 M NH_3 resulting in the separation of a tan solid. The aqueous mixture was then shaken with sufficient fresh ether to dissolve the solid. The aqueous residue was discarded, and the ether was evaporated to yield 12 g (61%) of the crude ketone. This material was vacuum distilled (0.010 mm, bp 127°) and collected as a light yellow oil which crystallized on cooling as yellowish needles. The needles were dissolved in the minimum amount of a hot mixture of n-pentane — dichloromethane (3:1) and recrystallized at dry ice temperature as white needles melting at 42 — 43°.

Phenyl-4-pyridylketone (4-benzoylpyridine). This ketone was prepared in accord with the method employed for the synthesis of 4-fluorophenyl-2-pyridylketone (p. 20). The Grignard was prepared by the addition of 50 ml (74 g, 0.47 mol) bromobenzene dissolved in 75 ml ether to 10 g (0.42 mol) of activated magnesium which was covered with 50 ml ether. Following the addition of the bromobenzene solution the reaction mixture was refluxed with stirring for 2 hours.

A mixture of 21 g (0.20 mol) 4-cyanopyridine (isonicotinonitrile) in 200 ml ether was refluxed until the nitrile dissolved. This solution was then added dropwise to the cooled Grignard (-40°). This resulted in the immediate formation of a tan solid, and the reaction mixture was stirred vigorously to prevent lumping. The ketimine intermediate was cooled to -55° and hydrolyzed by the addition of 50 ml ice-cold saturated aqueous NH_4Cl. This was followed by the addition of 100 ml concd HCl at 0°, resulting in the formation of much rust-

colored solid. The further addition of acid (100 ml 6 M HCl) dissolved this solid. The ether layer was separated and discarded. Adjustment of the pH of the aqueous phase by the careful addition of concd NH_3 resulted in the separation of copious quantities of a yellow precipitate. This material was dissolved in the minimum amount of fresh ether. Evaporation of the ether yielded 34 g (93%) of the ketone, a well defined crystalline yellow solid, which melted at 68 -- 70°.

4-Methylphenyl-4-pyridylketone (p-tolyl-4-pyridylketone). This material was prepared in the same manner as 4-fluorophenyl-2-pyridylketone (p. 20). The Grignard was prepared by the addition of 17 ml (24 g, 0.14 mol) p-bromotoluene dissolved in 100 ml ether to 3.7 g (0.15 mol) activated magnesium covered with 50 ml ether. Following the complete addition of the aryl halide solution the reaction mixture was refluxed for 2 hours and then cooled to -10°. This resulted in the separation of a brown precipitate so the Grignard was not cooled further. A filtered solution of 10 g (0.10 mol) 4-cyanopyridine in 100 ml ether was added dropwise with stirring resulting in the formation of a large amount of tan solid. Warming of this mixture to ambient temperature did not cause the solid to dissolve. The ether phase was drawn off by aspiration through a coarse frit filtering stick to remove unreacted 4-cyanopyridine. The reaction mixture was recooled to 0° while stirring, and hydrolysis was effected by the dropwise addition of 50 ml ice-cold saturated aqueous NH_4Br. This was followed by the addition of 60 ml 2 M HCl, and the mixture was allowed to stand until the unreacted magnesium had dissolved completely. More acid was added as needed to insure that the pH of the aqueous phase was less than 1.

The aqueous phase was now washed twice with 200-ml portions of fresh ether. The ether washes were discarded, and the aqueous phase was adjusted to pH 7 by the careful addition of 6 M NH_3. This resulted in the separation of a considerable amount of white precipitate. This material was shaken with sufficient ether to effect dissolution. Evaporation of the ether yielded 14 g (71%) of the yellowish ketone which melted at 86 – 89°.

4-Methoxyphenyl-4-pyridylketone. (This material had been prepared previously by Bhattacharyya and Stoufer (7) in accord with the method of LaForge (23). For the sake of completeness its preparation is given below.)

A solution of 51 ml (74 g, 0.40 mol) p-bromoanisole (1-bromo-4-methoxybenzene) dissolved in 160 ml ether was added dropwise over a period of 1 hour at ambient temperature to 9.6 g (0.40 mol) of activated magnesium. The reaction mixture was stirred vigorously throughout and refluxed for 1 hour following the addition of the bromoanisole. The Grignard was then cooled in an ice bath, and to this was added dropwise a solution of 21 g (0.20 mol) 4-cyanopyridine in 400 ml ether. The reaction mixture was stirred constantly throughout. Following the addition of the 4-cyanopyridine, the reaction mixture was refluxed for 1 hour and then cooled in an ice bath to 0°. Hydrolysis was effected by the careful addition of 50 ml ice-cold saturated aqueous NH_4Cl. The ether and aqueous layers were then separated, and the aqueous layer was twice extracted with 100-ml portions of fresh ether. The ether extracts were combined with the original ether layer. The ether fraction was extracted thrice with 200-ml portions of 3 M HCl. The aqueous

fractions were pooled and extracted thrice with 100-ml portions of fresh ether. All ether fractions were now discarded, and the aqueous fraction was boiled for 1 hour to ensure complete ketimine decomposition. The aqueous fraction was cooled and carefully neutralized with ice-cold 3 M NaOH resulting in the separation of a yellow precipitate. This material was filtered, washed with fresh deionized water, and air dried. The crude ketone was then dissolved in 100 ml hot chloroform. This solution was treated while hot with anhydrous $MgSO_4$ and filtered. The volume of the chloroform filtrate was tripled by the addition of fresh ether and cooled for 1 hour. The reprecipitated solid was filtered, washed with ice-cold ether, and air dried to yield 28 g (71%) of the yellowish ketone which melted at 123 – 124°.

2-Pyridylphenyl-4-fluorophenylmethanol. Magnesium turnings (8.1 g, 0.33 mol) were placed into the dry reaction flask, and a small crystal of iodine was added. The flask was carefully heated with a heating mantle until the iodine just vaporized whereupon heating was discontinued. As the iodine recondensed the magnesium turnings were stirred briefly to ensure the deposition of a reasonably homogeneous layer of iodine onto the surface of the metal. A solution of 32 ml (51 g, 0.29 mol) 4-bromofluorobenzene in 200 ml ether was added dropwise to the activated magnesium. The reaction mixture was stirred continuously as it was warmed to reflux. Reflux was continued for 2 hours following the addition of the aryl halide, and the reaction mixture was then cooled to -60°. A solution of 11 g (0.060 mol) phenyl-2-pyridylketone (2-benzoylpyridine) dissolved in 300 ml ether was added dropwise to the stirred Grignard. The cooling bath was removed periodically to

minimize the freezing out of materials from the reaction mixture. As the ketone solution was added the reaction mixture became red-violet in color. Following the addition of the ketone solution the cooling bath was removed, and the contents of the flask were stirred until a temperature of -10° was attained. During this time the reaction mixture became dark brown in color. The addition product was hydrolyzed at -10° by the careful addition of 25 ml ice water resulting in the formation of a lemon-yellow ether layer and a pink aqueous layer. The aqueous layer was discarded, and the ether layer was extracted thrice with 200 — ml portions of 3 M HCl. The extracted ether layer was discarded, and the aqueous phase was adjusted to pH 7 — 8 by the careful addition of 6 M NH_3. This resulted in the separation of a yellow-orange solid. The solid — aqueous mixture was shaken with sufficient fresh ether to dissolve all the solid. The aqueous portion was then discarded, and the ether solution was combined with 3A molecular sieves until incipient crystallization was observed. The sieves were removed, and the ether evaporated completely to yield 13 g (77%) of the crude yellow-orange carbinol. This solid was dissolved in 200 ml hot methanol and treated with 6 g of wood charcoal. This mixture was refluxed 30 minutes and filtered. The hot, yellow methanol solution was allowed to stand until crystallization of a yellow solid occurred. The carbinol exhibited a melting range of 79 — 82°.

Anal.: Calcd for $C_{18}H_{14}NOF$: C, 77.40; H, 5.05; N, 5.02.

Found: C, 77.51; H, 5.10; N, 5.16.

2-Pyridyl-4-methylphenyl-4-fluorophenylmethanol. The Grignard was prepared exactly as was that for 2-pyridylphenyl-4-fluorophenylmethanol

(above) employing 8.1 g (0.33 mol) magnesium turnings and 31 ml (49 g, 0.28 mol) 4-bromofluorobenzene. The reaction mixture was then cooled to -50°, and a solution of 10 g (0.051 mol) 4-methylphenyl-2-pyridyl-ketone dissolved in 250 ml ether was added dropwise to the stirred Grignard. This resulted in the formation of a butterscotch-colored dispersion. Following the addition of the ketone the cooling bath was removed, and the reaction mixture was stirred until a temperature of 10° was reached. The reaction mixture was recooled to -10° and hydrolyzed by the dropwise addition of 200 ml ice-cold saturated aqueous NH_4Cl. This resulted initially in the formation of a white slurry which slowly became a yellowish emulsion. The emulsion was broken by filtering through glass wool followed by squeezing through coarse filter paper. The yellow ether layer was then extracted thrice with 100 — ml portions of 6 M HCl. The ether phase was discarded, and the aqueous portions were combined and treated carefully with 6 M NH_3 until pH 7 was attained. This resulted in the separation of a sticky yellowish oil. The oil was extracted with the minimum volume of fresh ether, and the aqueous residue was discarded. Evaporation of the ether again resulted in separation of the oil. Characterization of the oil (12 g, 82%) revealed it to be the desired carbinol. The oil was vacuum distilled (0.010 mm, bp range 160 — 170°); but the collected distillate remained as a light yellow oil after cooling.

Anal.: Calcd for $C_{19}H_{16}NOF$: C, 77.75; H, 5.56; N, 4.77.

Found: C, 77.87; H, 5.56; N, 4.60.

2-Pyridyl-4-methoxyphenyl-4-fluorophenylmethanol. A solution of 5.4 ml (9.4 g, 0.050 mol) p-bromoanisole in 25 ml ether was added

dropwise with stirring to 1.3 g (0.053 mol) activated magnesium covered with 25 ml ether. The reaction mixture was heated to gentle reflux, and the formation of Grignard was evidenced by the development of a grey-brown translucency. Following reflux for a period of 2 hours Grignard formation appeared to be complete. The reaction mixture was now cooled to -5° with an ice — salt bath, and to this a solution of 6.0 g (0.030 mol) 4-fluorophenyl-2-pyridylketone dissolved in 120 ml ether was added dropwise with continuous stirring. During this addition of ketone a yellow solid settled out. Following the addition of ketone the cooling bath was removed, and stirring was continued as the reaction mixture slowly warmed to ambient temperature. This resulted in the formation of a light tan-colored suspension with traces of reddish-purple material dispersed throughout. The reaction mixture was subsequently heated to reflux for a period of 1 hour and then cooled. The bulk of the ethereal solution was removed from the reaction flask by aspiration through a coarse frit filtering stick. The material which remained in the flask was washed three times with 50 -- ml portions of fresh ether. The ether washes were removed by aspiration and combined with the original ether layer. Upon standing a white semisolid material separated from the ether. The residual reaction mixture was now hydrolyzed at 0° by the careful addition of 50 ml saturated aqueous NH_4Br, followed by 150 ml 1 M HCl. This resulted in the separation of a yellow oil. The aqueous phase was adjusted to pH 7 by the careful addition of 3 M NH_3. This produced a milky dispersion of the oil. The aqueous phase was then shaken with fresh ether until the dispersion cleared, and the aqueous layer was drawn off and discarded. The aspirated ether portions (above) were filtered

through a medium frit to separate the white semisolid material. The ether filtrate was discarded, and the white material was hydrolyzed on the frit by the addition of a few ml deionized water. This produced more of the yellow oil. The oil was dissolved in fresh ether, and the oil -- ether solutions were combined. Evaporation of the ether yielded 6.2 g (67%) of the oily carbinol. Repeated attempts to crystallize this material were unsuccessful. An accurate mass for the molecular ion of the carbinol was determined mass spectrally. Calcd for $C_{19}H_{16}NO_2F$: 309.1164. Found: 309.1170 (mean of four determinations; deviation, ±2 ppm).

4-Pyridylphenyl-4-fluorophenylmethanol. A solution of 12 ml (18 g, 0.10 mol) 4-bromofluorobenzene in 50 ml ether was added dropwise to 2.4 g (0.10 mol) ether-covered activated magnesium. Stirring was continuous during the addition of the aryl halide, and Grignard formation ensued upon gentle warming of the reaction flask as evidenced by the development of a grey-brown dispersion and the ebullition of ether. After the aryl halide had been added the reaction mixture was stirred and refluxed for a period of 2 hours. Subsequently, the reaction mixture was cooled to -5°, and a filtered solution of 11 g (0.60 mol) phenyl-4-pyridylketone dissolved in the minimum amount of ether (ca. 200 ml) was added dropwise. This resulted in the immediate formation of a pink solid. Vigorous stirring was maintained to insure uniform mixing. Stirring was stopped following the addition of ketone, and the mixture stood at ambient temperature for a period of 12 hours. The bulk of the ether phase was now drawn off by aspiration through

a coarse frit filtering stick and discarded. The residual solid was washed twice with fresh 50 — ml portions of ether, and the washes were discarded. The solid was subsequently recooled to -5° and hydrolyzed with stirring by the dropwise addition of 100 ml saturated ice-cold aqueous NH_4Br. This was followed by the addition of 1 M HCl until a pH of 5 — 6 was attained. The aqueous mixture was now transferred to a large separatory funnel and shaken with 400 ml ether. The aqueous (lower) layer was tan in color, and the ether (upper) layer was yellow. A small quantity of semisolid yellow material resided at the interface of the liquid layers. The aqueous layer was drawn off, and the semisolid was combined with the ether layer and together shaken with four separate 150 -- ml portions of 2 M HCl. This resulted in the dissolution of most of the solid and a translucent ether layer. Evaporation of the ether yielded a small amount of brown material which was discarded. All of the aqueous portions were then pooled resulting in the development of an opaque dispersion. Treatment of the aqueous layer with 6 M NH_3 produced initially a clearing of the opaqueness, and as the pH was raised to 4 — 5 much white solid separated. The solid was isolated by filtration and the filtrate again treated with 6 M NH_3 to bring the pH to 7. This resulted in the separation of more white solid which was also filtered off. All of the aqueous filtrate was discarded, and the combined solid samples were air dried to yield 15 g (92%) of product which exhibited decomposition to a brownish oil at 185 — 190°. To convert any hydrochloride salt to free carbinol the entire amount of white solid was slurried with 100 ml 1 M NH_3. After standing for 1 hour the solid was separated by suction filtration, washed with 200 ml of deionized water and air dried. The

isolated material was a finely divided white solid which melted at 192 -- 194° without appreciable discoloration.

Anal.: Calcd for $C_{18}H_{14}NOF$: C, 77.40; H, 5.05; N, 5.02.

Found: C, 77.13; H, 5.09; N, 5.00.

An accurate mass for the molecular ion of the carbinol was determined mass spectrally. Calcd for $C_{18}H_{14}NOF$: 279.1058. Found: 279.1052 (mean of five determinations; deviation, ±2 ppm).

4-Pyridyl-4-methylphenyl-4-fluorophenylmethanol. The preparation of this carbinol was carried out by the method used for the preparation of 4-pyridylphenyl-4-fluorophenylmethanol (above). The quantities of materials employed were: 2.9 g (0.12 mol) magnesium; 14 ml (21 g, 0.12 mol) 4-bromofluorobenzene dissolved in 50 ml ether; and a filtered solution of 7.4 g (0.038 mol) 4-methylphenyl-4-pyridylketone dissolved in 125 ml ether.

Following hydrolysis the aqueous phase was adjusted to pH 1 with 1 M HCl resulting in the separation of 5 — 10 ml of a brown oil. This oil was drawn off; the work-up of the oil is given below. The acidic aqueous phase was twice shaken with 400 — ml portions of fresh ether. Each shaking resulted in the separation of a small quantity of yellowish semisolid material. This material and the ether extracts were discarded. The aqueous phase was neutralized by the careful addition of 6 M NH_3. This resulted in the separation of a yellowish solid which was isolated by suction filtration. Characterization of the solid (4.4 g) revealed that it was the crude carbinol. The brown oil (above) was stirred with 300 ml 1 M HCl resulting in the formation of a brown

creamy emulsion. The emulsion was extracted thrice with 100 — ml portions of ether. This removed the translucency from the aqueous layer which was now a light yellow solution. All the organic washes were discarded, and the aqueous layer was neutralized by the careful addition of 6 M NH_3. This resulted in the separation of a yellowish solid which was filtered, washed with deionized water, and air dried to yield 1.2 g of solid which melted at 169 — 172°. This material, combined with the previously isolated solid, afforded a yield of 50%.

Anal.: Calcd for $C_{19}H_{16}NOF$: C, 77.75; H, 5.56; N, 4.77.

Found: C, 77.60; H, 5.55; N, 4.82.

An accurate mass for the molecular ion of the carbinol was determined mass spectrally. Calcd for $C_{19}H_{16}NOF$: 293.1215. Found: 293.1216 (mean of three determinations; deviation, ±0.3 ppm).

4-Pyridyl-4-methoxyphenyl-4-fluorophenylmethanol. The Grignard was prepared exactly as was that for 4-pyridylphenyl-4-fluorophenyl-methanol (p. 29) using 1.3 g (0.53 mol) magnesium; and 60 ml (9.0 g, 0.51 mol) 4-bromofluorobenzene dissolved in 30 ml ether. To this at -5° was added in 100 — ml increments a solution of 5.5 g (0.25 mol) 4-methoxyphenyl-4-pyridylketone dissolved in 600 ml ether. As the ketone solution contacted the reaction mixture a yellow solid formed and separated. Following the addition of ketone the stirred reaction mixture was refluxed for 90 minutes and was then set aside and not disturbed for a period of 12 hours. The reaction mixture was now a yellow creamy dispersion, and little of the ethereal liquid phase could be drawn off by suction through the glass filtering stick. Therefore, the reaction mixture was cooled to -5° and hydrolyzed by

the dropwise addition of 50 ml of saturated ice-cold aqueous NH_4Br, followed by the addition of 100 ml 1 M HCl. This resulted in the dispersion of a brown oily material in the aqueous phase. The ether layer was extracted four times with 125 — ml portions of 1 M HCl and then discarded. The aqueous portions were pooled yielding a yellow-green opaque mixture. This mixture was adjusted to pH 7 by the careful addition of 6 M NH_3, and upon standing for 2 — 3 hours a quantity of light tan solid separated. The solid was filtered, air dried, and dissolved in a refluxing mixture of 100 ml 4:1 ethylacetate — acetone. After standing 72 hours, this solution was reduced to a volume of ca. 30 ml by evaporation which resulted in the separation of a white crystalline solid. The crystals were filtered, washed with a few ml of ice-cold ether, and air dried to yield 4.0 g (41%) of the carbinol melting at 181 — 183°.

Anal.: Calcd for $C_{19}H_{16}NO_2F$: C, 73.77; H, 5.21; N, 4.53.
Found: C, 73.75; H, 5.26; N, 4.51.

An accurate mass for the molecular ion of the carbinol was determined mass spectrally. Calcd for $C_{19}H_{16}NOF$: 309.1164. Found: 309.1167 (mean of six determinations; deviation, ±1 ppm).

The Purification of Diphenyl-4-pyridylmethane. The commercially obtained alkane (mp 120 — 125°) was found to be contaminated by trace amounts of the corresponding diphenyl-4-pyridylcarbinol (from which the alkane was probably prepared). This was demonstrated by treating a sample of the "alkane" with 70% $HClO_4$ which produced color characteristic of alcohol ionization. A visible spectrum of this acid solution gave band positions identical to those got for a similar (known) solution of diphenyl-4-pyridylcarbinol.

A glass column (20 cm x 2 cm i.d.) was fitted with a stopcock above which was inserted a plug of glass wool covered with a 1 cm thick sand mat. The vertically supported column was filled ca. half full with reagent hexane, and the stopcock was opened slightly to permit the dropwise outflow of solvent. A hexane slurry of freshly activated 80 — 200 mesh alumina (Brockman Activity I) was poured into the column, and as the alumina settled on the sand mat the column was carefully agitated to insure uniform adsorbent deposition. A 0.5 cm thick sand mat was added to the top of the alumina layer in the packed column, and the level of solvent was adjusted to coincide with the top of the sand mat. A saturated solution of the alkane was prepared by stirring 2 g of the alkane into 6 ml benzene. This solution was filtered and carefully placed on the column. Gravity elution was carried out by the dropwise percolation of the following solvents: 1) 250 ml 1:1 hexane — benzene; 2) — 5) 500 — ml portions of ether. Each of the ether fractions 2 — 4 was evaporated separately yielding ca. equal quantities of a white solid. A small portion of each of these samples of solid was treated with 70% $HClO_4$. In each instance the resulting solution was virtually colorless. These samples of solid were combined and dissolved in the minimum amount of hot methanol. Crystallization afforded a yield of 1.0 g of well developed white needles which melted at 125 — 126°. A solution of these needles in 70% $HClO_4$ was transparent in the visible region of the spectrum.

Synthesis of Complexes

I. The Preparation of the "bis" Alcohol Complexes of Palladium(II), $[Pd(II)(pyLOH)_2Cl_2]$.

Dichlorobis(4-pyridylphenyl-4-fluorophenylmethanol)palladium(II). Palladium chloride powder (0.16 g, 9.3×10^{-4} mol) was placed in a 250-ml round bottom flask together with 0.10 g (2.4×10^{-3} mol) dry lithium chloride and 100 ml acetone. The mixture was stirred magnetically and gently refluxed until all solids had dissolved (ca. 24 hours). The solution which resulted was deep red-brown in color. To this solution 0.51 g (1.8×10^{-3} mol) of solid 4-pyridylphenyl-4-fluorophenylmethanol was added; immediately the red-brown color changed to yellow-orange. The yellow-orange solution was refluxed for 24 hours while stirring. Acetone was then removed by distillation until a solution volume of ca. 20 ml was attained. The reaction mixture was filtered through a medium frit, transferred to a small beaker, and treated with 5 ml of deionized water. A yellow crystalline precipitate developed during standing for 1 hour. The precipitate was isolated by suction filtration through a medium frit, washed on the filter with three 10 — ml portions of fresh deionized water, and oven dried on the filter at 130°. The solid was then washed from the filter with 50 ml fresh acetone yielding a yellow solution. This solution was flooded with sufficient n-pentane to produce permanent cloudiness and was then allowed to stand until crystal formation occurred. A yield of 0.15 g (20%) of well defined yellow needles was obtained. The product exhibited darkening at >260° and decomposed to a black oil at 295°.

Anal.: Calcd for $C_{36}H_{28}N_2O_2F_2PdCl_2$: C, 58.75; H, 3.83; N, 3.81.
Found: C, 58.73; H, 4.03; N, 3.70.

Dichlorobis(4-pyridyl-4-methylphenyl-4-fluorophenylmethanol)-palladium(II). The material was prepared in exactly the same fashion as for the preparation of the bis(4-pyridylphenyl) complex (above) using 0.53 g (1.8×10^{-3} mol) 4-pyridyl-4-methylphenyl-4-fluorophenylmethanol. A yield of 0.17 g (22%) of well defined yellow needles was obtained. The product exhibited darkening at >240° and decomposed to a black oil at >260°.

Anal.: Calcd for $C_{38}H_{32}N_2O_2F_2PdCl_2$: C, 59.74; H, 4.22; N, 3.67.
Found: C, 60.26; H, 4.33; N, 3.49.

Dichlorobis(4-pyridyl-4-methoxyphenyl-4-fluorophenylmethanol)-palladium(II). This material was prepared in exactly the same fashion as for the preparation of the bis(4-pyridylphenyl) complex (above) using 0.56 g (1.8×10^{-3} mol) 4-pyridyl-4-methoxyphenyl-4-fluorophenylmethanol. A yield of 0.16 g (20%) of well defined yellow needles was obtained. The product exhibited darkening at >240° and decomposed to a black oil at 250°.

Anal.: Calcd for $C_{38}H_{32}N_2O_4F_2PdCl_2$: C, 57.34; H, 4.05; N, 3.52.
Found: C, 57.90; H, 4.21; N, 3.38.

Dichlorobis(2-pyridyl-4-methylphenyl-4-fluorophenylmethanol)palladium(II). This material was not amenable to the thermodynamic investigations which were carried out in this work. (See Results and Discussion, p. 97). However, for the sake of completeness, its preparation is given.

It is the only well defined "2-pyridyl" complex which was isolated.] In actuality this material was obtained as a side product of the synthetic method which had been designed for the preparation of the "salt-like" complex (Z^+, $PdLCl_3^-$), where Z^+ is a suitable cation, and L is the pyridylmethanol.

Palladium chloride powder (0.28 g, 1.6×10^{-3} mol) was placed in a 250-ml round bottom flask together with 0.072 g (1.7×10^{-3} mol) dry lithium chloride, 0.47 g (1.6×10^{-3} mol) 2-pyridyl-4-methylphenyl-4-fluorophenylmethanol, and 50 ml acetone. This mixture was stirred magnetically as it was refluxed for a period of 2 hours resulting in the dissolution of all solids and the formation of a deep red-brown solution. The acetone was then removed by distillation yielding some red gummy material. The gummy semisolid was redissolved by the addition of 10 ml fresh acetone reproducing the red-brown solution. A heaping microspatula of tetramethylammonium chloride was dissolved in a mixture of 2 ml acetone and 1 ml methanol. This colorless salt solution was added to the red-brown solution (above) producing no apparent change. The addition of 2 ml dichloromethane induced the separation of a reddish oily material which clung to the inner walls of the flask. After standing overnight the oily material had failed to crystallize and was redissolved by the further addition of 20 ml fresh acetone. This solution was heated; following 30 minutes reflux a salmon-colored crystalline solid separated with the solution phase now being yellow-orange in color. A second microspatula of tetramethylammonium chloride was added, and the reaction mixture was returned to reflux for a period of 2 hours. After cooling, the salmon-colored solid was separated by filtration. (This solid was later shown to be tetramethylammonium tetrachloropalladate(II).) The

yellow-orange acetone filtrate was flooded with deionized water resulting in the separation of a yellow crystalline solid. This solid was filtered by suction through a medium frit, washed with deionized water, and air dried to yield 0.52 g (43%) of a material characterized as the "bis" alcohol complex (PdL_2Cl_2). This material decomposed to a black oil above 195°.

Anal.: Calcd for $C_{38}H_{32}N_2O_2F_2PdCl_2$: C, 59.74; H, 4.22; N, 3.67.
Found: C, 59.56; H, 4.39; N, 3.70.

II. The Preparation of the "Mono" Alcohol Complexes of Palladium(II), [Pd(II)(pyLOH)(L_N)Cl_2], where L_N is Diphenyl-4-pyridylmethane. (See also p. 33).

The Preparation of Pd(II)(pyLOH)(L_N)Cl_2, where pyLOH is 4-Pyridylphenyl-4-fluorophenylmethanol. In a dry environment 0.01 g (5.6×10^{-4} mol) palladium chloride powder was transferred to a 250-ml round bottom flask together with 0.16 g (5.8×10^{-4} mol) dried tetra-n-butylammonium chloride and 100 ml acetone. This mixture was stirred magnetically as it was refluxed for 72 hours to dissolve all solids, producing a deep red-brown solution. To this solution was added 0.14 g (5.7×10^{-4} mol) purified diphenyl-4-pyridylmethane (p. 33). As the alkane dissolved the color of the solution changed from red-brown to red-orange. This solution was refluxed for 2 hours and cooled. To this was added 0.16 g (5.7×10^{-4} mol) 4-pyridylphenyl-4-fluorophenylmethanol; as the alcohol dissolved, the color of the solution changed from red-orange to yellow-orange. This solution was refluxed for 1 hour after which acetone was removed by distillation until a solution volume of ca. 30 ml was attained.

The mixture was now distinctly yellow with incipient precipitation of a yellow solid having begun. Sufficient deionized water (ca. 10 ml) was added until permanent cloudiness was produced. The mixture was allowed to stand 48 hours to promote crystal growth, and was then filtered by suction through a tared frit (medium). The collected yellow solid was washed with deionized water and dried on the frit at 130° for a period of 1 hour. A yield of 0.35 g (89%) of well defined yellow needles was obtained. This material darkened above 245° and decomposed to a black oil above 270°.

Anal.: Calcd for $C_{36}H_{29}N_2OFPdCl_2$: C, 61.60; H, 4.16; N, 3.99.
Found: C, 61.34; H, 3.93; N, 3.83.

The Preparation of Pd(II)(pyLOH)(L_N)Cl_2, where pyLOH is 4-Pyridyl-4-methylphenyl-4-fluorophenylmethanol. This complex was prepared in exactly the same fashion as that for the 4-pyridylphenyl-4-fluorophenylmethanol complex (above). The same quantities of materials were employed together with 0.17 g (5.7×10^{-4} mol) 4-pyridyl-4-methylphenyl-4-fluorophenylmethanol. A yield of 0.35 g (87%) of well defined yellow needles was obtained. This material decomposed to a brown-black oil above 245°.

Anal.: Calcd for $C_{37}H_{31}N_2OFPdCl_2$: C, 62.07; H, 4.36; N, 3.91.
Found: C, 62.20; H, 4.32; N, 3.77.

The Preparation of Pd(II)(pyLOH)(L_N)Cl_2, where pyLOH is 4-Pyridyl-4-methoxyphenyl-4-fluorophenylmethanol. This complex was prepared in exactly the same fashion as that for the 4-pyridylphenyl-4-fluorophenylmethanol complex (above). The same quantities of materials were employed

together with 0.18 g (5.7×10^{-4} mol) 4-pyridyl-4-methoxyphenyl-4-fluorophenylmethanol. A yield of 0.35 g (84%) of well defined yellow needles was obtained. This material darkened above 180° and decomposed to a brown oil above 210°.

Anal.: Calcd for $C_{37}H_{31}N_2O_2FPdCl_2$: C, 60.71; H, 4.27; N, 3.83.
Found: C, 60.94; H, 4.46; N, 3.83.

Tetra-n-butylammonium Trichloro-(4-pyridylphenyl-4-fluorophenylmethanol)-palladate(II). This "salt-like" complex was prepared separately in order to establish the fact that it was a stable, isolable intermediate. (See Results and Discussion, p. 58.)

In a dry environment 0.12 g (4.3×10^{-4} mol) tetra-n-butylammonium chloride, 0.075 g (4.2×10^{-4} mol) palladium chloride powder, and 100 ml acetone were placed together in a 250-ml round bottom flask. This mixture was stirred magnetically as it was refluxed for a period of 24 hours. The reaction mixture now consisted of a deep red-brown solution phase containing traces of undissolved white and red-brown solids. The solution phase was carefully decanted into a clean flask, and to this was added 0.12 g (4.2×10^{-4} mol) 4-pyridylphenyl-4-fluorophenylmethanol. As the alcohol dissolved the solution changed color from red-brown to orange. This mixture was stirred magnetically at ambient temperature for a period of 1 hour and was then heated to reflux. Acetone was removed by distillation during reflux until a solution volume of ca. 30 ml was attained. To the hot red-orange acetone solution was added 30 ml ether, and this solution was allowed to cool without stirring. To the cooled solution n-pentane was added in small portions until permanent cloudiness was attained. Upon stirring for a period of a few hours a

small quantity of yellow-orange crystals developed and settled to the bottom of the flask. The solution phase, which was now slightly yellow, was treated again with n-pentane to reinduce cloudiness. After standing overnight the mixture was gravity filtered through a fluted filter, and the virtually colorless filtrate was discarded. The crystals which were collected were air dried, examined under a microscope, and found to be thin, transparent gold-orange sheet-like needles. This material melted at 150° to a red-brown oil. A yield of 0.29 g (94%, as based on palladium) was obtained.

Anal.: Calcd for $C_{34}H_{50}N_2OFPdCl_3$: C, 55.60; H, 6.86; N, 3.81.
Found: C, 55.35; H, 6.87; N, 3.77.

Elemental Analyses

Carbon, hydrogen, and nitrogen elemental analyses for ligands and complexes were performed either by PCR Incorporated, P. O. Box 466, Gainesville, FL, 32601, or by Atlantic Microlab, Incorporated, P. O. Box 54306, Atlanta, GA, 30308. No special handling techniques were required for either the ligands or the complexes.

Reagents and Solvents

The special, commercially obtained reagents which were employed in this research are listed in Table I (p. 42). These materials were used without further purification unless otherwise specified. The

Table I
Special, Commercially Obtained Reagents - - and Suppliers

Reagent	Supplier
p-bromoanisole (1-bromo-4-methoxybenzene)	Aldrich Chemical Co., Inc., Milwaukee, WI, 53233
4-bromofluorobenzene	Aldrich
2-bromopyridine	Aldrich
2-cyanopyridine (picolinonitrile)	Aldrich
4-cyanopyridine (isonicotinonitrile)	Aldrich
diphenyl-4-pyridylcarbinol	K & K Laboratories, Inc., Plainview, NY, 11803
diphenyl-4-pyridylmethane	Aldrich
phenyl-2-pyridylketone (2-benzoylpyridine)	Aldrich
tetra-n-butylammonium chloride	Eastman Kodak Co., Rochester, NY, 14650
p-tolunitrile (p-methylbenzonitrile)	Aldrich

additional reagents and solvents which were employed were readily available, reagent grade quality materials, and were used without further purification.

Instrumental Analytical Methods

Proton Magnetic Resonance Spectra. The ^{1}H nmr spectra were obtained using a Varian Associates Model A-60A nmr spectrometer operating at 60 MHz. The spectra were taken as saturated carbon tetrachloride solutions using tetramethylsilane (TMS) as internal standard. The spectra were examined principally with respect to integrated peak intensity ratios for the purposes of ascertaining sample homogeneity and molecular composition.

Mass Spectra. Mass spectra were obtained using an AEI MS-30 mass spectrometer equipped with a DS-30 data system. Solid and oil samples were introduced into the ionization chamber *via* direct insertion probe at 200° and run at an ionizing voltage of 70 eV.

Infrared Spectra. The IR spectra were obtained using a Perkin-Elmer Model 337-B grating infrared spectrophotometer scanning the region 4000 -- 400 cm^{-1}. Solid samples were intimately ground with oven dried reagent potassium bromide and run as pressed semimicro discs. Oily samples were run as follows: A neat potassium bromide disc was pressed and supported horizontally. The oil was warmed until it became fluid, and a drop of the oil was added to the surface of the salt disc. This technique deposited the oil as a uniform thin film on the disc. The spectrum was recorded as soon as the oil cooled sufficiently to become viscous.

The IR spectra were used to provide evidence of ligand homogeneity by establishing the absence of a carbonyl stretching vibration (ketone),

the presence of a hydroxyl band (alcohol), and to confirm the presence of both ligands in the "mixed" mono-alcohol complexes (pp. 38-40).

Fluorine Magnetic Resonance Spectra. The ^{19}F nmr spectra were obtained using a Varian Associates Model XL-100-15 nmr spectrometer operating at 94.1 MHz in either continuous wave or Fourier transform pulse mode. Fourier transform capabilities were provided with a Nicolet TT-100 computer system equipped with a 16 K capacity memory. All spectra were recorded using external H_2O as a lock signal. Fluorine resonances were recorded relative to 10% $CFCl_3$ in acetone and to neat trifluoroacetic acid as external reference standards. Operation at a sweep width of 5000 Hz afforded an uncertainty of ±15 Hz (±0.16 ppm) in the position of observed ^{19}F signals.

Ligand spectra were recorded as 0.05 M acetone solutions, as 0.05 M 10% $HClO_4$ solutions, and as saturated 70% $HClO_4$ solutions. Spectra of complexes were recorded as saturated acetone solutions and as saturated 70% $HClO_4$ solutions. All solutions were filtered through a coarse frit directly into the nmr sample tube just prior to recording of spectra. $HClO_4$ solution spectra of the complexes were run in large capacity nmr tubes employing Fourier transform techniques exclusively to facilitate signal detection for these very dilute samples. All samples were air cooled in the sample holder during the recording of spectra in order to maintain ambient temperature.

Visible Spectra and Molar Absorptivity Coefficient Determination. Visible spectra were obtained using a Beckman Model DB-G grating spectrophotometer equipped with a Sargent Model SR recorder. Molar absorptivity

coefficients (c, Table II, p. 77) were determined for carbenium ion species derived from each of the free and complexed alcohols dissolved in 70% $HClO_4$. Samples of appropriate size (10^{-4} to 10^{-5} g) were weighed to three significant figures using a Cahn Model 1501 Gram Electrobalance calibrated in the 1 mg range. Oily samples had to be weighed by difference. This was done by taring a small finely drawn glass whisker and then carefully touching the glass whisker to the oil until a very small bit of the oil adhered to the whisker. The weight of the oil was obtained from the combined weight of the oil and whisker. The weighed samples were stirred in ca. 9 ml of the acid to complete dissolution and then made to 10.0 ml with fresh acid. These acid solutions were scanned vs. the neat acid as blank spanning the region 760 — 320 nm to ascertain the position of λ_{max} for the various carbenium ion species. Each ionic species exhibited two main absorption bands with the more intense band appearing at lower energy. If the absorption maxima were "off-scale", the acid solutions were diluted with the necessary quantity of fresh acid to produce "on-scale" readings within acceptable sensitivity limitations of the spectrophotometer readout, viz., >10% T (<1.0 absorbance units).

Visible Spectra and the "Deno" Titration Technique. The equilibrium constant (K_{R^+}) datum pertaining to the thermodynamic stability of each of the carbenium species which have been considered in this work was experimentally obtained as follows: a 70% $HClO_4$ solution of the alcohol (ligand) or complex under investigation was prepared and diluted (if necessary) with fresh acid until an "on-scale" (viz., 15 — 25% T) spectrophotometer reading was obtained with the instrument set at λ_{max}

for that particular ionic species. It is not necessary to fix the concentration of this solution. (See Results and Discussion, p. 92.) A predetermined quantity of this solution (ca. 5 g) was weighed to five significant figures into the special cuvette (described below). (By employing the same sample size for each titration, data treatment was greatly simplified.) In order to obtain exactly the same weight for each sample, very minute quantities of the parent acid solution could be transferred to or from (as necessary) the contents of the cuvette with the tip of a finely drawn glass rod. The acid solution in the special cuvette was then transferred to the cell compartment of the spectrophotometer and "read" at λ_{max} relative to a sample of the neat acid used as blank. The cell compartment was thermostatted at 20 – 25° by the circulation of tap water. The special cuvette was removed from the cell compartment, and the parent acid solution of the carbenium ion was diluted by the addition of a measured increment (ca. 0.02 – 0.08 g) of deionized water from the special burette (described below). Following each addition of water the acid solution was carefully mixed in the cuvette; the cuvette was returned to the spectrometer, and the absorbance reread. This procedure was repeated until the absorbance of the acid solution had fallen off considerably (<0.20 absorbance units) thereby indicating a reconversion of carbenium ion to alcohol (or complexed alcohol) precursor in excess of 50%. Data treatment is considered in Results and Discussion (pp. 83-103).

The specific gravity (ρ) of the reagent 70% $HClO_4$ was determined before performing the titrations by weighing accurately (5 sig. fig.) a measured volume of the acid in a 10 ml volumetric flask which had been volumetrically calibrated (to 4 sig. fig.) with a weighed sample

of distilled water. Prior to calibration the neck of the flask was heated and drawn to a fine bore of sufficiently large inner diameter to permit insertion of a Pasteur pipette for liquid transferral. The flask was then calibrated by marking the drawn neck at a volume dictated by the weighed sample of water contained in the flask. Specific gravity data for water at ambient conditions were used to calculate the volume of the flask at the calibration mark.

Special Cuvette. A 1.00 cm path length quartz cell fitted with a quartz/Pyrex graded seal stem was obtained from Pyrocell Manufacturing Co., Inc., Westwood, NJ, 07675. The stem was shortened so that the cell fitted conveniently into the sample compartment of the spectrometer. A standard taper size 13 ground glass neck was added to the top of the stem to facilitate the direct dropwise addition of water to the acid solution of the carbenium ion contained in the body of the cell during titration. A side arm of ca. 4 ml capacity was fused to the stem at an angle of ca. 75° to the cell. Thus the thorough mixing of water with the acid solution during titration was readily accomplished by rocking the cell after each addition of water through an angle of 90°. This particular cell design also eliminated any problems associated with sample loss upon removal of the cell stopper prior to each addition of titrant (water) since none of the liquid sample was in contact with the stopper throughout the titration.

Special Burette. A 5.00 ml capacity semimicro burette equipped with an automatic refilling reservoir and side arm was fitted with a 5 cm length of surgical tubing at the drip tip. A 12 cm length of 6 mm (o.d.)

capillary tubing was drawn to a very fine bore pipette tip at one end. The opposite end of the capillary was inserted snugly into the open end of the surgical tubing. A small screw clamp was affixed to the surgical tubing. With the stopcock opened on the burette, the screw clamp was adjusted until drops of uniform size were discharged at a convenient rate from the drip tip of the capillary. It was found that during a titrimetric run (ca. 30 minutes) drops of water could be collected from this burette assembly which differed in weight by not more than ±0.0002 g for drops averaging 0.0190 to 0.0230 g, provided the tip of the capillary was wetted prior to drop size calibration. This obviated the need to weigh the sample in the cell following each addition of water; that is, it was necessary only to count the number of drops collected in order to determine the total quantity of added water at any given time during the titration.

RESULTS AND DISCUSSION

Synthetic Consideration

On the Preparation of Ligands. The pyridine alcohol carbenium ion precursors employed as ligands in this work were found to be conveniently preparable by the Grignard reagent synthetic routes, outlined in the experimental section. It was discovered, however, that consistently better yields of product were obtained when the Grignard reagent was prepared from 4-bromofluorobenzene followed by the addition of the appropriate pyridyl ketone. That is, in attempts to prepare the identical alcohol from a 4-fluorophenylpyridylketone and the required phenyl-type Grignard, much poorer yields were got. These results suggest that 4-bromofluorobenzene Grignard was readily prepared in good yield as a reactive intermediate and was a sufficiently potent carbanionic reagent to attack the carbonyl carbon of the ketone. The difficulties encountered in the alternate synthetic route leading to acceptable quantities of product are attributed to the preparation in poor yield of the necessary Grignard intermediate. This was particularly obvious in the case for which 4-methylphenyl Grignard or 4-methoxyphenyl Grignard were the required carbanion. Thus, ketones prepared from these Grignards could usually be obtained only in poor yield. None the less this was not a problem of consequence since the desired material (the ketone) was

easily separated from the unreacted starting materials. However, the separation of alcohol from parent ketone was very difficult, and it was necessary therefore to convert ketone precursor to alcohol as completely as possible in order to isolate the desired alcohol as a ketone-free product. Thus, the preparative route for the alcohols employing 4-bromofluorobenzene Grignard was the better method.

The filter stick filtration technique employed prior to hydrolysis in the synthetic procedures for the preparation of alcohols facilitated the removal of unreacted ketone from the reaction mixture. This technique utilized the fact that the ketone — Grignard addition compound was sparingly soluble in the ether solvent whereas the ketone itself was moderately to readily soluble. Therefore prior to hydrolysis unreacted ketone which was dissolved in the ether layer could be drawn off by suction through the filter stick. Repeated washings of the reaction mixture with fresh ether, followed by filter stick filtration, afforded essentially complete removal of unreacted ketone.

On the Choice of Palladium(II). The most obvious reason for the incorporation of palladium(II) as the central metal species into the complexes considered in this research is to permit a direct and immediate extension upon the related work of previous investigators. Richardson (6) and Wentz (8) both pointed out the suitability of palladium(II) to such investigations owing to its low oxidation state and high penultimate d-orbital occupancy. These factors would be expected to contribute to metal stabilization of a coordinated carbenium ion *via* back donation of metal 4d electron density into the π-framework of the carbenium ion provided the ligand donor atom and carbenium ion carbon atom were both

members of the ligand π-system. The relative inertness of palladium(II) complexes also suggests that such complexes would be amenable to these types of studies. Finally, the diamagnetic nature of 4-coordinate palladium(II) stemming from its square planar complex geometry, makes it convenient for nmr investigations on the stability of a coordinated carbenium ion since no paramagnetic contribution to measured chemical shifts would be observed.

On the Selection and Preparation of Complexes. The results of previous investigations of bis palladium(II) complexes of ionizable pyridyl and thiazolyl alcohols demonstrated the suitability of coordinated carbenium ions derived from these complexes for thermodynamic stability studies upon such ions. Therefore, the bis palladium(II) complexes were prepared in order to enlarge the scope of earlier work through similar studies upon carbenium ions derived from the fluorine-tagged pyridylmethanols.

The palladium(II) complexes containing but one ionizable ligand molecule per complex were prepared so that a one-to-one relationship could be established between a coordinated carbenium ion and the stabilizing effects exerted by the metal-containing moiety. Indeed, the development of such a synthetic method would in itself be a novel contribution to that area of preparative coordination chemistry embodying palladium(II) as the central metal species. This follows in that there are known many "mixed" neutral complexes of palladium(II) of the type $[Pd(II)XYL_1L_2]$, where X and Y are anionic groups, and L_1 and L_2 are neutral donor ligands. In none of these complexes, however, are the L ligands pyridine homologs; rather they are usually donors which exhibit particularly strong π-acid character. Examples of those ligands

which are usually found in these complexes are PR_3 (R = alkyl or aryl), SR_2, CO, and various alkenes. Actually, work has been reported concerning the preparation of such mixed complexes wherein pyridine donors have been incorporated into the coordination sphere as neutral ligands, but the bulk of this work has focused upon the use of platinum(II) as the central metal species.

In 1936 Mann and Purdie (24) reported the preparation of mixed complexes of palladium(II) having the general formula $[Pd(II)(Bu_3P)(am)Cl_2]$, where Bu_3P is tri-n-butylphosphine, and am is either aniline, p-toluidine, or pyridine. These complexes were obtained *via* the initial preparation of the binuclear chloride-bridged *trans* bis(Bu_3P) complex $[Pd_2(Bu_3P)_2Cl_4]$, followed by cleavage of the chloride bridges with the required molar ratio of the amine of choice. However, an examination of the information cited in the experimental section of this article revealed that accounts are given only for the preparation of the complexes which incorporated aniline and p-toluidine as the nitrogen donors. Investigations by Chatt and Venanzi (25) in 1957 upon similar complexes of palladium(II) again served to demonstrate that the neutral chloride-bridged, binuclear compounds could be converted to the corresponding mononuclear complexes *via* rupture of the bridging bonds of the halide ions with triphenylphosphine. The parent bridged materials had been preparable with di-n-pentylamine or piperidine as the nitrogen donor ligands in *trans* positions; but these workers reported that they were not able to obtain the related bridged compounds using pyridine or pyridine-containing ligands. Obviously, therefore, neutral mononuclear complexes with pyridine in the coordination sphere had not been isolated during these investigations. In 1969 Chatt and Mingos (26) reported

the successful preparation of neutral, square planar, mixed, mononuclear complexes of palladium(II) which had pyridine included within the coordination sphere of the metal. Again the synthetic route to these mixed mononuclear materials relied upon the cleavage of bridging bonds in binuclear precursors wherein the bridging species were either chloride ions or p-toluenesulfinate ions. In 1975 Boschi and coworkers (27) succeeded in preparing some neutral, square planar, mixed, mononuclear complexes of palladium(II) with coordinated pyridine. They also employed a chloride-bridged binuclear precursor $[Pd_2L_2Cl_4]$ wherein the neutral L groups were aromatic isonitriles. Treatment of the bridged compound with the required molar ratio of pyridine afforded the isolation, in good yield, of the corresponding trans mononuclear complex. The results of both of these studies (viz., Chatt and Mingos, and Boschi and co-workers) therefore indicated that a general route towards the synthesis of mixed mononuclear complexes of palladium(II) which included pyridine-type ligands required initially the preparation of a suitable halide-bridged binuclear complex, followed by the rupture of the bridging bonds with the selected pyridine donor(s).

So, in order to obtain the desired pyridine-containing, mixed mononuclear complexes in this research, it was first attempted to prepare the binuclear chloride-bridged dimeric materials $[Pd_2L_2Cl_4]$ with the L groups as the pyridine methanols. This method depended upon the direct combination of the mononuclear bis-alcohol complexes $[PdL_2Cl_2]$ with the complex anion $[PdCl_4]^{2-}$ on a 1:1 mole basis with respect to palladium. The bridged dimer, however, could not be obtained by this method. Therefore, the chloride bridged complex $[Pd_2L_2Cl_4]$ with triphenylphosphine (Ph_3P) ligands incorporated as the neutral L groups was

prepared according to the method outlined by Chatt and Venanzi (25). The Ph_3P was employed because of its structural similarity to the pyridylmethanols. This bridged material, which was a red-brown solid, was slurried in refluxing acetone and treated with 4-pyridyl-4-fluorophenylmethanol (4-pyLOH) on a 1:1 mole basis with respect to palladium. As reflux was continued (ca. 3 hours) the bridged material dissolved and a yellow solution resulted. When this solution was saturated with n-pentane a pale yellow crystalline solid settled out. Characterization of this solid indicated that the desired mixed mononuclear complex $[Pd(II)(Ph_3P)(4\text{-pyLOH})Cl_2]$ had been obtained. This result suggested that the problem of preparing the mononuclear mixed complexes containing the pyridine alcohols had been solved. However, when this material was treated with 70% $HClO_4$ for the purpose of carrying out stability investigations upon the "coordinated" carbenium ion it was discovered that the coordinate bond between the ionized pyridine alcohol and the palladium metal center was quickly ruptured (ca. 5 minutes or less). It was presumed that this bond breaking was a consequence of the effective trans labilizing effect exerted by the strong π-acid ligand, triphenylphosphine. This result therefore dictated the necessity to prepare the mixed mononuclear complexes with a neutral, nonionizable counter ligand, which would not exhibit particularly strong π-acid behavior in these complexes. The selection of 4-pyridyldiphenylmethane as an appropriate counter ligand was clearly a good choice. This is attributable to the structural comparability of the alkane to the pyridine alcohols, and to the anticipated similarity in chemical behavior of the alkane to pyridine itself. Thus, the problem at hand was the development of a synthetic procedure through which a molecule of the alcohol as well as a molecule

of the alkane could be systematically introduced into the coordination sphere of the metal in the mononuclear complex. The following considerations were pertinent: 1) The inability to prepare the chloride-bridged binuclear complexes containing pyridine donors in trans positions [$Pd_2(pyLOH)_2Cl_4$] (vide supra) ruled out the use of such a material as a precursor. The bridging bonds in this dimer would presumably have been susceptible to attack by the "second" pyridine donor thereby yielding the mixed pyridine mononuclear complex. 2) In view of the anticipated similarity in donor character of the pyridine alkane to the pyridine alcohols there appeared to be no method by which these two pyridine ligands could be added directly to the palladium metal center in the required stoichiometric ratio.

The synthetic finds of Goodfellow, Goggin, and Duddell (28) provided reasonable prospects for the preparation of the desired complexes. These workers recognized that there are many complex anions of the type $[Pt(II)LCl_3]^-$ (L = C_2H_4, CO, NO, NH_3, or pyridine; references for the preparation of this complex anion with these respective ligands are cited in this article) which are well known. They discovered that such complex anions were also preparable with L as PR_3, SR_2, or AsR_3 (R = alkyl or aryl), and that a similar series of complexes (excluding pyridine) was preparable as well with palladium(II). This was the first general account given for the successful preparation of such types of complex anions of palladium(II). The usual synthetic route which these workers employed was characterized by refluxing the chloride-bridged, binuclear material [$M_2L_2Cl_4$], M equals Pt(II) or Pd(II), with the required stoichiometric quantity of tetra-n-propylammonium chloride in an inert organic solvent such as dichloromethane. The complex anion which

was formed upon rupture of the chloride bridges was apparently stabilized in solution by the large tetraalkylammonium counterion. The complex anion was found to be isolable as the tetraalkylammonium salt *via* treatment of the dichloromethane reaction mixture with excess ether which resulted in crystallization of the desired product. The salient aspect of this preparative method is that it permitted the controlled inclusion of a particular neutral ligand into the coordination sphere of the metal atom. However, as previously indicated, this particular method was not directly applicable to the situation involving the pyridine donors since the necessary bridged precursors with *trans* pyridine donors had not been preparable. Nevertheless, further considerations paralleling this synthetic approach were certainly warranted in that this technique served to reinforce the possibility of being able to investigate stability relationships between the metal center and a singly charged coordinated pyridine carbenium ion provided $[Pd(II)LCl_3]^-$ complex anions of the pyridine alcohols could be prepared.

Goodfellow, Goggin, and Duddell had also reported the preparation of the anionic complexes $[Pd(II)(C_2H_4)Cl_3]^-$, and $[Pd(II)(CO)Cl_3]^-$, by reacting the binuclear anion $[Pd_2Cl_6]^{2-}$ with the required molar quantity of the neutral ligand in the presence of tetra-*n*-butylammonium ion using *cis*-1,2-dichloroethylene as solvent. Again treatment of the reaction mixture with excess ether induced the separation of the desired product as a crystalline solid. Infrared spectroscopic investigations by Adams and coworkers (29) also served to indicate the potential usefulness of the binuclear anion $[Pd_2Cl_6]^{2-}$ as a precursor to mononuclear complexes of palladium(II) of the type $[Pd(II)LCl_3]^-$ by demonstrating

that the force constant for the terminal metal-halide stretching vibration was greater than that for the bridging metal-halide vibration. Thus, it would be expected that the dimeric anion $[Pd_2Cl_6]^{2-}$ would be attacked at the bridging positions by incoming ligands.

It appeared, therefore, to be reasonable to treat polychloropalladate(II) anions with the pyridine alcohols in an appropriate solvent in the presence of tetraalkylammonium cations with the anticipation of sustaining the stability of the $[Pd(II)(pyLOH)Cl_3]^-$ complex anions. In conjunction with this, palladium chloride powder was stirred in refluxing acetone with tetramethylammonium chloride (tMACl) on a 1:2 mole basis. A red-orange solution initially resulted as the solids began to dissolve, but as reflux was continued the color of the solution disappeared and a salmon-colored solid separated. This solid was slurried with 4-pyridylphenyl-4-fluorophenylmethanol in refluxing solvent but no additional change occurred. Nevertheless, the incipient formation of the red-orange solution indicated the presence of a solution-stable chloroanion of palladium(II). Further investigations indicated that the solution-stable species was $[Pd_2Cl_6]^{2-}$ and that the salmon-colored solid was the acetone-insoluble salt $[(tMA)_2PdCl_4]$. Thus, the nature of the palladium(II) polychloroanion was dependent upon the concentration of the ammonium salt. Studies by Henry and Marks (30) upon glacial acetic acid solutions of palladium(II) in the presence of various alkali metal chlorides served to indicate that with readily soluble chlorides such as LiCl, $[PdCl_4]^{2-}$ was the commonly encountered palladium(II) anion, whereas with moderately soluble chlorides such as NaCl, the binuclear species $[Pd_2Cl_6]^{2-}$ was got. Therefore, it appeared that regulation of the tetraalkylammonium chloride concentration

afforded a method by which the nature of the palladium(II) polychloro-anion could be controlled. The combination of palladium chloride powder with tMACl (1:1) in refluxing acetone did in fact yield complete dissolution of all solids and a stable red-orange solution. Treatment of this solution with a typical 4-pyridylmethanol (1:1 with respect to palladium) again resulted in the separation of a salmon-colored precipitate [$(tMA)_2PdCl_4$] and a yellow solution. Workup of the yellow solution yielded the bis-alcohol complex [$Pd(II)(pyLOH)_2Cl_2$]. Thus, the tMA cation did not appear to be capable of stabilizing the desired anionic mono-alcohol complex regardless of the nature of the polychloro-palladate(II) precursor.

Palladium chloride powder was then combined with tetra-n-butyl-ammonium chloride (1:1) in refluxing acetone again resulting in the dissolution of all solids and a stable red-orange solution. Treatment of this solution with a typical 4-pyridine methanol (1:1 with respect to palladium) induced an immediate color change in the solution from red-orange to yellow-orange with the separation of no solids. Workup of this solution (see Experimental p. 40) revealed that the desired anionic complex [$Pd(II)(4\text{-}pyLOH)Cl_3$]$^-$ had been obtained. Further studies showed that this anionic complex was readily converted to the desired mixed, neutral, mononuclear complex by treatment (1:1) with the 4-pyridyl alkane in acetone solution (see Experimental pp. 38-40).

(Note: During the course of this research all synthetic procedures involving palladium(II) were run using acetone as solvent. There are many standard methods for the preparation of complexes of palladium(II) employing alcohol (usually methanol or ethanol) as solvent, but in this work it was discovered that in the presence of alcohol palladium(II)

was frequently reduced to palladium black. No similar difficulty was encountered with acetone.)

On the Suitability of 4-Pyridyldiphenylmethane as a Counterligand in the Mixed Complexes. As reported previously (see Experimental p. 33) the commercially obtained alkane was found to be contaminated with trace quantities of the corresponding 4-pyridyl alcohol. To be sure that the alkane was not converted to the alcohol (carbenium ion) via oxidation in 70% $HClO_4$, a solution of the purified alkane in the acid was stirred at ambient temperature in the open environment of the laboratory. After stirring for a period of 2 hours this solution was scanned in the visible region of the spectrum and was found to be transparent. Therefore no complications were expected to arise during thermodynamic studies upon complexes which contained the alkane since all such measurements were made within a 2 hour time span.

The similarity in donor behavior of the alkane to the 4-pyridyl alcohols was demonstrated by the preparation of the anionic complexes $[PdLCl_3]^-$ (in situ) with either the alkane or the alcohol, followed by conversion to the mixed complex. Thus, the mixed complexes were preparable independent of the order of addition of the respective pyridine donors.

Finally, a small sample of mixed complex (any) was triturated in 70% $HClO_4$ for a period of ca. 1 hour. The acid was removed by filtration and the residue was washed with deionized water and dried. An IR scan of the residue revealed it to be of the same constituency as the original mixed complex. This indicated that both pyridine ligands remained coordinated during thermodynamic stability investigations and

again demonstrated the suitability of 4-pyridyldiphenylmethane as an appropriate counterligand. When the complex $[Pd(II)(Ph_3P)(4\text{-pyLOH})Cl_2]$ had been treated in a similar fashion (i.e., triturated in 70% $HClO_4$) it was found that the pyridine ligand (carbenium ion) was discharged from the complex (p. 54).

Concerning Carbenium Ion Salts. Various synthetic routes are available for the preparation of stable salts of trityl-type carbenium ions (see, for instance, the methods given in the papers by Sharp and Sheppard (31), by Dauben et al. (32), or by Olah et al. (33)). It may certainly prove to be interesting and profitable to investigate the stability of the free and complexed carbenium ions which have been dealt with in this work as discrete salt-like species in aprotic, nonreactive solvents. Current considerations however, have exclusively involved the use of 70% $HClO_4$ as an ionizing medium in order to provide a direct extension to previous work upon trityl-type carbenium ions derived from the pyridyldiphenylmethanols.

Thermodynamic Investigations and Measurements

Electronic Spectra and Carbenium Ion Constitution and Structure. Considerable work has been done on the electronic spectra of trityl-type carbenium ions in the 200 – 750 nm (50.0 – 13.3 kK) spectral region. The majority of this work, however, has been focused upon the transitions exhibited by these ions in a rather limited portion of this region, viz. 300 – 550 nm (33.3 – 18.2 kK), because the electronic bands found

here are those which are characteristic solely of the carbenium ion. The higher energy transitions (50.0 – 33.3 kK) exhibited by these ions are normally present in the spectrum of the precursor molecules (i.e., tertiary alcohols) and are characteristic of the electronic absorptions of the isolated conjugated systems which are bound to the carbinol carbon in the unionized alcohol. Previous electronic absorption studies on these types of ions (e.g., Richardson (6) and Wentz (8)) including similar studies performed during the course of this work have demonstrated that the higher energy (ultraviolet) spectral region of these alcohols remains virtually unchanged for a given alcohol independent of the nature of the solvent. Thus, the significant electronic changes which occur in these systems upon carbenium ion generation are not directly reflected by these higher energy transitions. The dramatic changes which do take place in the electronic spectrum of these alcohols upon ion formation are illustrated by the development of two intense (ϵ_{max} ca. $10^4 - 10^5$ liter mol^{-1} cm^{-1}), broad absorption bands ordinarily appearing between 300 and 550 nm. This spectral region is transparent for the alcohols dissolved in a nonionizing solvent, e.g., acetone, alcohol, or 1 M $HClO_4$. The extreme intensities of these bands are expected for strongly allowed $n \leftarrow \pi$ charge transfer type transitions. As pointed out by Dunn (34) based upon considerations of the classical theoretical work of Mulliken (35) on electronic spectroscopy, the intensity of a charge transfer band is expectably large since the charge transfer phenomenon occurs over at least one interatomic distance in the absorbing species. Thus, the radius vector ($\underline{r}$) of the transition is relatively large. Since the magnitude of the transition moment integral is directly proportional to $\underline{r}$, and in turn directly

proportional to the oscillator strength (f) of the transition, f must also be large. Hence, the intensity of the transition is considerable. The general positions of these trityl-ion charge transfer bands have been rationalized by considering that alcohol ionization is accompanied by the conversion of the system from a quasi even-alternant benzene hydrocarbon to an odd-alternant, fully conjugated benzene hydrocarbon. According to various workers (see, for instance, Deno et al. (36)) based on simple LCAO MO calculations this transformation introduces a zero energy (nonbonding) π-symmetry orbital into the molecular orbital scheme of the previously unionized alcohol intermediate between the highest energy filled π-orbitals and the lowest energy unfilled π^*-orbitals. Thus, the energy of the longest wavelength (lowest energy) electronic transition observed for these ionic species should be on the order of half the energy of the longest wavelength transition exhibited by benzene, the model compound. Since the wavelength of this transition for benzene is 256 nm it is expected that the longest wavelength electronic transition of the trityl-type ions would appear in the vicinity of 512 nm. As pointed out by Richardson (6:153) the rather inexact nature of this treatment is revealed by the fact that the longest wavelength electronic absorption exhibited by triphenylcarbenium ion is 431 nm (in 96% H_2SO_4) which is at considerably shorter wavelength than that predicted from the benzene model.

An eclectic account of previous investigations upon the electronic nature of arylcarbenium ions reveals that extensive considerations have been made, but that these considerations are not without certain perplexing aspects. In 1932 Schoepfle and Ryan (37) reported that the two substances, triphenylchloromethane and methyldiphenylchloromethane, yield

essentially the same visible spectrum when dissolved in dichloroethylene in the presence of stannic chloride. This prompted Newman and Deno (38) to conclude that this was evidence indicating that in triarylcarbenium ions no more than two (and perhaps just one) of the aryl rings could simultaneously participate in resonance interactions with the carbenium ion center (the exocyclic carbon atom). Completely synchronous resonance stabilization of a triarylcarbenium ion involving all of the aryl rings would of course require an all-planar molecular ion configuration of D_{3h} symmetry. Lewis et al. (39) had already reported as a consequence of studies on crystal violet ion (tris-(dimethyl-p-aminophenyl)-methyl ion), that the all-planar configuration of the ion is not possible owing to steric interactions between the ortho hydrogen atoms on the phenyl rings. These workers had speculated on the existence of two isomers of the ion having structures akin to a symmetric and an asymmetric propeller wherein the phenyl rings were the blades of the propeller. The presence of two intense bands in the electronic spectrum of crystal violet ion supported the proposal that each of the two isomeric forms of the ion was a distinct chromophoric system. Additional evidence cited by Newman and Deno which suggested the structural uniqueness of trityl-type ions was the following. Tri-o-tolylcarbenium ion was reported to be as stable as tri-p-tolyl-carbenium ion and to exhibit essentially the same electronic spectrum. This was an unexpected result owing to the considerably greater degree of inhibition towards ring resonance stabilization of the ion anticipated for the tri-o-tolyl ion as a consequence of steric interaction between the o-methyl groups. Also, van't Hoff i-factor data on solutions of tri-p-dimethylaminophenylcarbinol in 100% H_2SO_4 indicated that even in this strongly acidic medium one of the p-amino groups was not protonated.

This suggested that only one of the rings was involved substantially in resonance stabilization with the cation center. Other investigations by Newman and Deno on the electronic spectra of various carbenium ions revealed that the observed band positions were sensitive to changes in phenyl ring substitution. Attempts to rationalize these band shifts premised mainly on resonance considerations were inconclusive. Further attempts to rationalize the observed differences in band intensity and position in the electronic spectra of various series of related aryl-carbenium ions by Deno, Jaruzelski, and Schriesheim (40), met with limited success. These workers discovered a systematic spectral trend characterized by an increase in λ_{max} as well as in band intensity resulting from singular substitution of any of the groups, $-N(CH_3)_2$, $-NH_2$, $-OCH_3$, or $-Cl$, into the para position on one of the phenyl rings in triphenylcarbenium ion. The trend appeared to coincide with expectations contingent upon simple extension of the π-electron donating, conjugated system of the substituted cation relative to the triphenyl ion. However, successive para substitution of these groups on subsequent phenyl rings in a given ion resulted in discontinuous shifts in $\bar{\nu}_{max}$ and in molar absorptivity. In 1954, Branch and Walba (41) studied the electronic spectra of various para-aminotriphenylcarbinols in 96% H_2SO_4. They reported that each of the carbinols which was converted to its corresponding carbenium ion upon dissolution in the acid exhibited two intense bands in the visible region of the spectrum which had not been found to be present in the spectrum of the parent carbinol. It is interesting to note, however, that these workers reported no such bands for tri-p-dimethylaminophenylcarbinol in the acid and concluded in this instance that carbenium ion formation had not occurred (cf. the results

of Newman and Deno (above) with respect to their investigations on this particular carbinol). Branch and Walba also isolated a trend in band position shifts from their data. They rationalized that increases in resonance stabilization of a given carbenium ion resulted in an increase in the frequency of the band associated with that particular carbenium ion chromophore. The simplest example of their consideration is illustrated by comparing the relative positions of $\bar{\nu}_{max}$ for the ionic species $(C_6H_5)_2CH^+$ and $(C_6H_5)_3C^+$ wherein $\bar{\nu}_{max}$(diphenyl ion) < $\bar{\nu}_{max}$(triphenyl ion). Branch and Walba had attributed this absorption to the $(C_6H_5)_2C^+$ chromophore. Thus, these workers concluded that resonance stabilization of the $(C_6H_5)_2C^+$ chromophore in the trityl ion by the presence of the "third" phenyl ring resulted in a blue shift of $\bar{\nu}_{max}$. Branch and Walba also contended that trityl carbenium ions exhibited two visible region absorption bands (instead of but one) because of two carbenium ion containing chromophores believed to exist in the sterically hindered parent ion. This was in basic agreement with similar considerations made previously by Lewis et al. (39). Related studies in this area by Evans and coworkers (42) provided evidence pointing to the existence of a relationship between band intensity and resonance interactions in triarylcarbenium ions. These investigators reported that para substitution of a given group on a phenyl ring in triphenylcarbenium ion resulted in a notable increase in ε for the main absorption band of that particular ion, whereas the corresponding ortho substitution of the same group resulted in a marked decrease in ε for the same band.

Studies by Dehl et al. (43), and by Deno et al. (36) served to invalidate a number of the earlier arguments concerning the interpretation of the electronic spectra of trityl carbenium ions. Dehl et al.

concluded from pmr investigations on various deuterated triphenylcarbenium ions that the three phenyl rings in the cationic aggregate were equivalent. This result suggested that analyses of the electronic spectra of such ions would require the attribution of any trityl carbenium ion chromophore to the ion as a whole, therefore denying the possibility of simultaneous existence of two (or more) chromophores in the molecular framework of the ion. Deno et al. performed simple LCAO MO calculations on aryl cations and found that the results of these calculations predicted identical $\bar{\nu}_{max}$ positions for the principal electronic absorption exhibited by related mono-, di-, and triaryl cations. Thus, inhibition of resonance in a sterically hindered carbenium ion would still leave $\bar{\nu}_{max}$ (calculated) unchanged. Also, these calculations indicated that the intensity of the principal absorption for such ions is invariant to phenyl ring rotation (due to steric interaction). Hence, these authors concluded that electronic absorptions exhibited by such ions could not be used as a measure of steric inhibition to resonance interaction existing within the ion. In yet a later article, Deno (44) has again pointed to the irresolute nature of the situation in commenting that much of the work on the electronic spectra of arylcarbenium ions still requires revision. Olah et al. (45), as well have concluded that there is a great deal of uncertainty in the literature citations concerning the visible and ultraviolet spectra of carbenium ions. Interestingly enough, however, in order to rationalize some of their results these workers employed the notion that in a sterically crowded triarylcarbenium ion only two of the aryl substituents are part of the absorbing chromophore, while the third functions as a cross-conjugating electron donor or acceptor moiety. So, once again the possiblity of the existence

of multiple chromophores in trityl-type carbenium ions is considered. Thus, as late as 1966, many of the problems resulting from unsatisfactory interpretation of the electronic spectra of carbenium ions remained.

To a large degree, recent investigations in this area rely heavily upon molecular orbital treatments of the electronic structure of aryl-carbenium ions. Streitwieser (46:226-230) has shown that in the HMO approximation the lowest energy transition exhibited by triphenyl-carbenium ion can be considered to be associated with the passage of an electron from the highest occupied bonding MO to the vacant nonbonding MO in the odd-alternant hydrocarbon created upon cation generation. To a first approximation the energy level diagram associated with this transition is the same as for the benzyl cation. Various, more sophisticated MO treatments (46:360-362) however, reflect the complex and imbroglietic nature of this approach to the problem by calculating rather grossly different charge densities for the π-framework carbon atoms in the ground state of the trityl ion.

By employing MO and resonance theory Waack and Doran (47) attempted to correlate the effects of methyl group substitution in odd-alternant anions with the resultant band shifts of the main absorption bands found in the electronic spectra of these ions. They noted that this type of substitution (i.e., methyl or alkyl) on an even-alternant hydrocarbon had - - in the absence of steric affects - - always induced a red shift in the electronic conjugation bands, whereas similar substitution on a nonalternant hydrocarbon had induced either a red or blue shift depending upon the site of substitution. They reported spectral changes for the odd-alternant anions to be similar to those for the nonalternants and experienced qualitative success in applying the

results of their calculations to the prediction of the spectral behavior of odd-alternant ions. A particular highlight of this effort was the prediction that α-alkyl substitution on an odd-alternant cation would result in a blue shift of $\bar{\nu}_{max}$ which is in agreement with reported data. A rather comprehensive MO treatment by Grinter and Mason (48) yielded a symmetry-based energy level diagram for structurally comparable arylmethyl ions. An examination of this energy level diagram revealed that the longest wavelength, lowest frequency transitions for a related bis- and trisarylmethyl ion pair should be approximately identical (cf. the conclusions reached by Deno et al. (36)). However, stemming from more acute considerations, these authors showed that the ground state charge stabilization of a given triaryl ion was greater than that for the corresponding bisaryl ion (recall the conclusions of Branch and Walba (41), pp. 64-65). Thus, the highest occupied bonding MO's for the trisaryl ion were somewhat lower in energy than the related MO's of the bisaryl ion, and therefore, the longest wavelength transition of the trisaryl ion was of slightly greater energy than the corresponding transition for the bisaryl ion. The dual nature of the visible region absorption envelope of the trisaryl ions was also considered by Grinter and Mason. Their explanation ran as follows. In the point group "C_3" (following from the anticipated propeller shape of these ions) the highest bonding MO's of the trisaryl ions are "five-fold degenerate," with the attendant symmetries e, e, and a_2. The MO's of the first excited state(s) are likewise five-fold degenerate, and are of a_1, a_1, a_2, and e symmetries. Again, provided that the ion is propeller shaped, transitions to the $^1A_2$ and ^1E excited terms are allowed and should be polarized parallel and perpendicular respectively,

to the principal three-fold symmetry axis of the ion. This appeared to be in basic agreement with similar considerations which had been made by Lewis and Bigeleisen (49) on the phenomenon of polarization upon the transitions in the electronic spectrum of crystal violet and malachite green. Thus, Grinter and Mason concluded that two low energy transitions of high intensity are expected (and are found) for such ions. (It is here appropriate to point out that results of newer studies on the electronic absorption spectra and magnetic circular dichroism (MCD) of triphenylcarbenium ions have suggested refinements of certain of the considerations made by Grinter and Mason. Mo et al. (50) found three MCD bands in the near UV, visible spectrum of triphenylcarbenium ion. This result indicated the existence of three electronic transitions in this spectral region for trityl-type carbenium ions whereas only two such bands were proposed to exist by Grinter and Mason. Dekkers and Kielman-van Luyt (51) in fact have stated that MO theory does predict three nearby singlet ← singlet transitions for a triaryl ion of D_3 symmetry. Two of these three transitions are to excited states of e symmetry and are polarized in the x,y-plane of the ion. (This plane is defined for an assumed coplanar arrangement of the aryl rings and the exocyclic carbon atom. Thus, the aryl rings are perpendicular to the principal symmetry axis of the molecular ion, the z-axis.) The third transition, however, which is to a state of a_2 symmetry and z-polarized, would not be observed if the cation were completely planar. Since the cation is propeller-shaped and not planar, this transition is observed (at slightly higher frequency than the higher energy intense band), but it is considerably weaker than either of the highly allowed transitions to the e states. It is also noteworthy that these investigators were not able to resolve

the two e state transitions which are observed to overlap rather severely (maxima are at 23.2 and 24.6 kK respectively with a reported ε of 38,700 for each band (45)). This suggests an inherent relationship between the electronic states in the ion from which these two bands originate. Consequences of this implication concerning the chromophoric nature of triarylcarbenium ions lie in the forthcoming text, vide infra.

It is now interesting and profitable to examine the wave functions for the molecular orbitals which were considered by Grinter and Mason to correspond to the energy levels which arise upon generation of a trisarylmethylcarbenium ion. The forms of these wave functions are:

$$\psi_I = a\phi_c + b(\psi_{aryl} + \psi_{aryl'} + \psi_{aryl''}) \qquad \{5\}$$

$$\psi_{II} = (\psi_{aryl} - \psi_{aryl'})/\sqrt{2} \qquad \{6\}$$

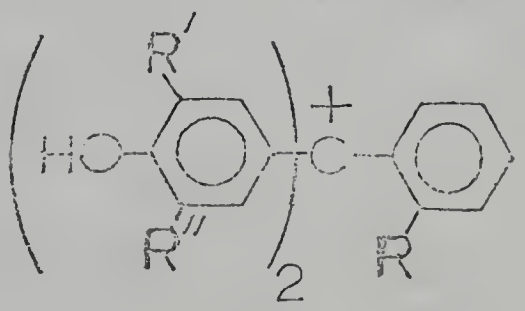
and

$$\psi_{II'} = (\psi_{aryl} + \psi_{aryl'} - 2\psi_{aryl''})/\sqrt{6} \qquad \{7\}$$

where ϕ_c is the wave function of the 2p state of the exocyclic carbon atom. The ψ_{II} functions represent the highest occupied bonding states of the ion, and their forms indicate that the bonding contribution of the "third" aryl ring ($\psi_{aryl''}$) is of principal significance in $\psi_{II'}$. (Note: The basic forms of these wave functions are virtually identical to the corresponding wave functions used in the calculations by Dekkers and Kielman-van Luyt (51).) Since the degeneracy of the ψ_{II} functions

has been removed to an appreciable degree by virtue of the nonplanarity of the ion (48) and by configuration interaction effects (46:227), (51), it follows that only one of the long wavelength, low energy transitions should reflect significant electronic contributions to carbenium ion stability (or instability, as the case may be) by the so-called "third" ring which is denoted above as aryl" in equations {5} and {7}. This consideration is given additional substance from the results of various investigations. Barker and coworkers (52) studied the electronic spectra of derivatives of malachite green produced by substitution in the "non-anilino" phenyl ring. They showed that the longest wavelength absorption band recorded for each derivative reflected primarily a flow of electrons from the two para-N,N-dimethyl substituted rings towards the exocyclic carbon atom. This is in keeping with MO calculations which have established that this carbon atom bears the principal degree of positive charge in the ground state of the ion (53), (an expected result). Therefore, replacement of the para-N,N-dimethyl groups with poorer electron releasing substituents resulted in a blue shift of $\bar{\nu}_{max}$. These workers also demonstrated the existence of a linear relationship between the appropriate Hammett constant for the phenyl ring substituent and the magnitude of shift in $\bar{\nu}_{max}$ induced by that particular substituent. Thus, a type of cross-conjugation seems to exist between the phenyl ring and the remainder of the conjugated system with respect to the energy of the longest wavelength transition. The results of studies by Hopkinson and Wyatt (54) concerning substituent effects upon the electronic absorptions of phenolphthalein monopositive ions (Figure 5) allowed these workers to conclude that $\bar{\nu}_{max}$ of the second longest electronic transition exhibited by these ions reflected primarily a shift in electron density

from the "third" ring towards the exocyclic carbon atom. In phenolphthalein this "third" ring is the ring to which the ortho-carboxylic acid group is attached. Hopkinson and Wyatt also compared the electronic absorption spectra of phenolphthalein and phenolsulphonphthalein and observed a considerable blue shift of the second band for the "sulpho" containing phthalein. This was expected owing to the appreciable electron withdrawing power of the sulphonic acid group. These results were corroborated via extended HMO calculations to resolve the electronic effects which arise from para-substitution of π-electron donating groups on two of the phenyl rings in triphenylcarbenium ion. Furthermore, the results of these calculations were found to be in agreement with the results of the HMO calculations which had been carried out by Mason and Grinter (48). These calculations also verified that such substitution of π-electron donating groups served to remove still further the degeneracy of the two highest occupied MO's in triaryl-type carbenium ions (see p. 70) with the higher energy occupied MO acquiring a greater



R = -COOH

R' = $-CH_3$, -Cl, -Br, etc.

R'' = $-CH_3$, -Cl, -Br, etc.

Fig. 5. Phenolphthalein monopositive ions

π-electron contribution from the rings which bear the more potent electron releasing substituents. Consequently, the conclusions reached which qualitatively associate the two principal electronic absorptions of triarylcarbenium ions with the MO's from which these transitions originate (p. 70) have been upheld. In addition, Hopkinson and Wyatt also isolated from their spectral data a linear variation between Hammett σ-meta substituent constants and shift magnitudes of the higher energy electronic band produced upon the substitution of groups ortho to the ring hydroxyl groups in phenolphthalein. Thus, whereas the results obtained by Barker and coworkers (52) indicated a cross-conjugation effect to exist upon the frequency of the lower energy band and the "third" aryl ring, Hopkinson and Wyatt showed a similar effect upon the frequency of the higher energy band by the two rings in a given triaryl-type carbenium ion which are the primary (as compared to the remaining ring) π-electron donating moieties.

Finally, it is still not clear whether the high intensity electronic absorption bands exhibited by triarylcarbenium ions may or may not be considered rigorously as charge transfer transitions! This concern is not crucial to the considerations made in this work; but for completeness a few remarks shall be tendered. Initially, in this discussion of electronic spectra, it was assumed rather tacitly that these electronic bands are charge transfer in nature (pp. 61-62). However, these absorptions do not meet with certain of the criteria (55) which have been employed for classifying electronic transitions as "charge transfer." Couch (56:65-66) for instance, has pointed out that the factors tending to indicate charge transfer interactions in monoaryl tropylium ions

(proved by Couch to exhibit intramolecular charge transfer) are either not present, or are opposite, in monoarylcarbenium ions. Furthermore, related studies by Couch (57:113-122) have suggested that triarylcarbenium ions as well do not exhibit bona fide charge transfer interactions. Dauben and Wilson (58) have at last demonstrated the existence of authentic charge transfer interactions for systems containing triarylcarbenium ions. They accomplished this via the preparation of various pyrene-triarylcarbenium ion complexes wherein the coordinated carbenium ion was found to function as a particularly potent π-acceptor. The electronic spectrum of any of these complexes gave a very intense band at relatively low energy (viz. 14.1 kK for coordinated triphenylcarbenium ion) which was not present in the spectrum of either component. These results imply that the existence of a "true" charge transfer interaction in a system requires an appreciable shift of electron density from a specific location in the ground state of the parent molecule (ion, etc.) to a new (and removed) location in the excited state. Perhaps then, it is in fact not extremely unrealistic to treat the principal electronic absorptions of arylcarbenium ions as charge transfer. Ramsey (55) has alluded to this assumption by suggesting that a charge transfer transition in a triarylborane can be associated with the promotion of an aryl ring π-electron into the empty available p orbital on the boron atom. Similarly, since the results of various studies on the electronic spectra of arylcarbenium ions have associated the main absorption bands with transfer of aryl ring π-electron density to the exocyclic carbon, these transitions may, at least broadly, be categorized as charge transfer. Arguments contrary to this classification can be registered based upon degree of charge transfer. For

instance, work by Olah et al. (59) on the pmr and ^{19}F nmr spectra of arylfluorocarbenium ions has demonstrated that the degree of charge delocalization into the aryl rings in these ions is substantial. Thus, electronic ground state charge delocalization in these ions appears to be considerable. Extended HMO calculations (54), however, have indicated an appreciable difference in carbon atom charge densities between the ground and first excited states in arylcarbenium ions. Let it suffice, therefore, to say that this aspect of arylcarbenium ion electronic spectral investigations remains largely a moot issue.

An examination of the electronic spectra and attendant data collected during this work is now in order. Examples of electronic spectra obtained for carbenium ions derived from a related series of compounds, namely pyLOH, Pd(II)(pyLOH)(L_N)Cl_2, and Pd(II)(pyLOH)$_2Cl_2$ (where pyLOH equals 4-pyridyl-4-methylphenyl-4-fluorophenylmethanol, and L_N equals diphenyl-4-pyridylmethane), have been presented in Figures 6 -- 8, p. 76. As these spectra are representative of all electronic spectra recorded for the carbenium ion species considered herein, no other electronic spectra are presented. Pertinent electronic spectral data are given in Table II, pp. 77-78).

The carbenium ion electronic spectra obtained in this work are found to be very similar to the related spectra (in the same spectral region) which have been reported by previous investigators (Richardson (6) and Wentz (8)). An examination of these spectra reveals the presence of two broad, intense absorption bands located within the 33.3 — 18.2 kK range. The lower energy band found in the spectrum of a given carbenium ion is always the more intense. The ε values reported in Table II indicate

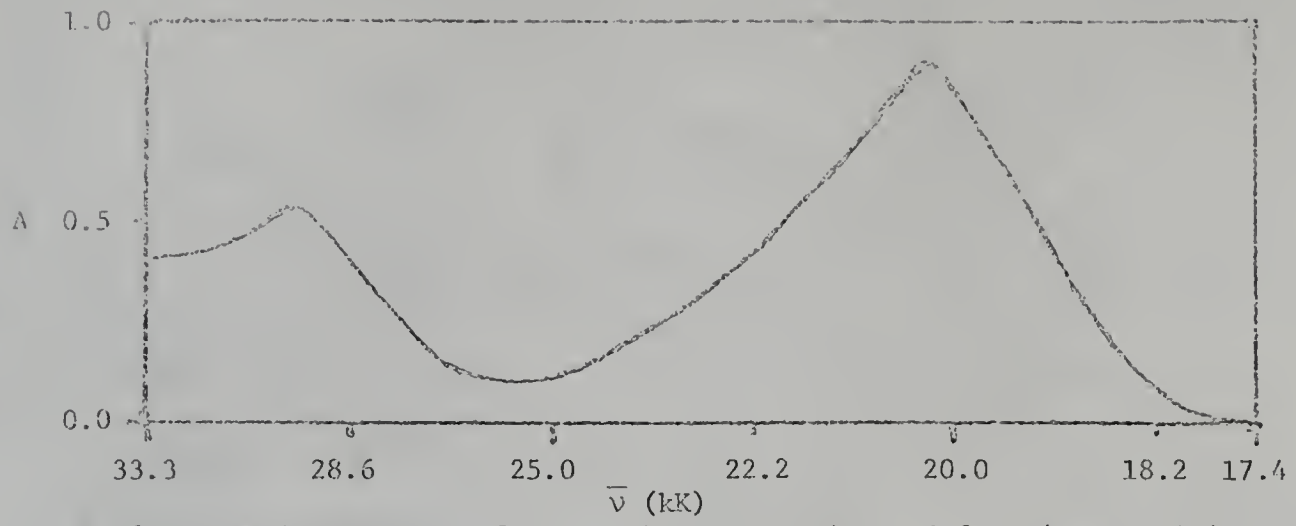


Fig. 6. Visible spectrum of the carbenium ion derived from 4-pyridyl-4-methylphenyl-4-fluorophenylmethanol, in 70% $HClO_4$. $\bar{\nu}_{max}$, 20.2, 29.7.

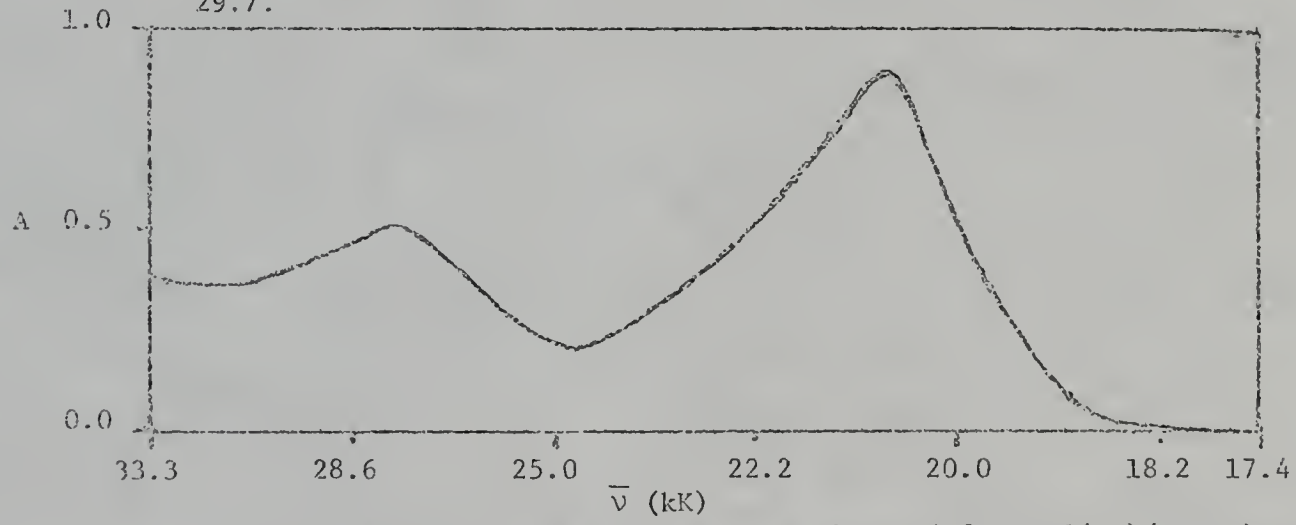


Fig. 7. Visible spectrum of the carbenium ion derived from Pd(II)(pyLOH)$(L_N)Cl_2$, where pyLOH is 4-pyridyl-4-methylphenyl-4-fluorophenyl-methanol, in 70% $HClO_4$. $\bar{\nu}_{max}$, 20.6, 27.6.

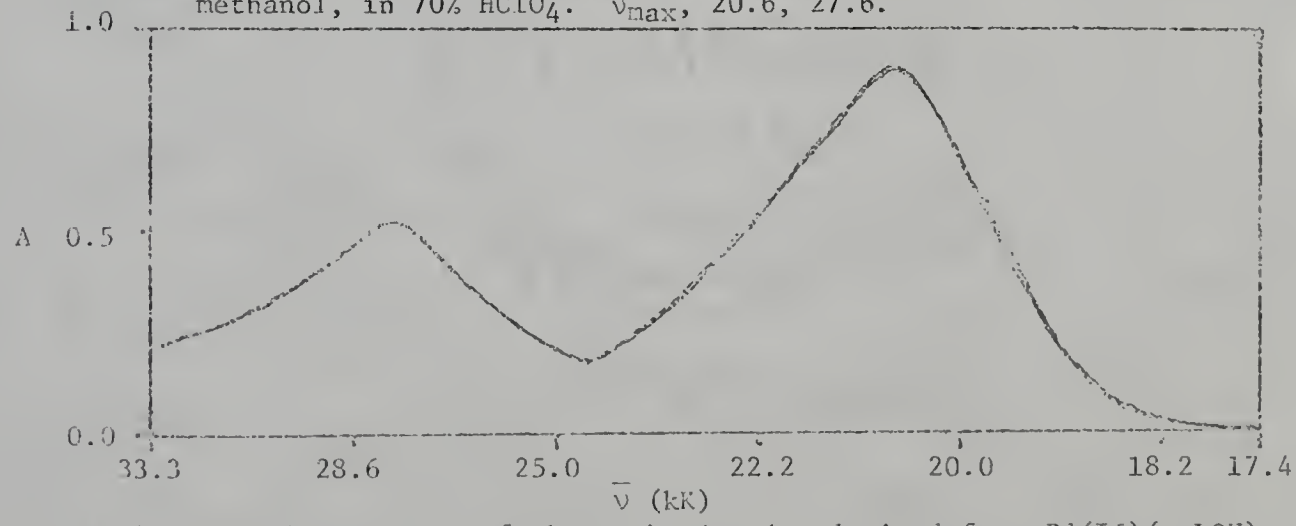


Fig. 8. Visible spectrum of the carbenium ion derived from Pd(II)$(pyLOH)_2$ Cl_2, where pyLOH is 4-pyridyl-4-methylphenyl-4-fluorophenyl-methanol, in 70% $HClO_4$. $\bar{\nu}_{max}$, 20.6, 27.7.

Table II
Electronic Spectral Data for the Various Carbenium Ion Species, in 70% $HClO_4$ at 25°

Carbenium Ion Precursor	λ_{max} (nm)		$\bar{\nu}$ (kK)		$\varepsilon \times 10^{-4}$ (l mol cm^{-1})		Cation Color (in 70% $HClO_4$)
	x-band	y-band	x-band	y-band	x-band	y-band	
Alcohols: 2-pyLOH = 2-pyridyl-R-4-fluorophenyl-methanol							
R = -phenyl	490	371	20.4	27.0	(2.73)	(1.32)[a]	orange-pink
R = -4-methylphenyl	507	373	19.7	26.8	4.56	1.75	red-pink
R = -4-methoxyphenyl	505	361	19.8	27.7	5.87	2.30	red-orange
Alcohols: 4-pyLOH = 4-pyridyl-R-4-fluorophenyl-methanol							
R = -phenyl	482	340	20.7	29.4	4.21	1.34	pale yellow
R = -4-methylphenyl	496	337	20.2	29.7	3.58	1.93	orange-pink
R = -4-methoxyphenyl	495	337	20.2	29.7	3.58	1.09	orange-pink

Table II — Extended

Carbenium Ion Precursor	λ_{max} (nm)		$\bar{\nu}$ (kK)		$\varepsilon \times 10^{-4}$ (l mol cm^{-1})		Cation Color (in 70% $HClO_4$)
	x-band	y-band	x-band	y-band	x-band	y-band	
Complexes: Pd(II)(4-pyLOH)$(L_N)Cl_2$							
R = -phenyl	471	357	21.2	28.0	-	- [b]	pale yellow
R = -4-methylphenyl	485	362	20.6	27.6	(2.28)	(1.12)[c]	yellow-gold
R = -4-methoxyphenyl	492	346	20.3	28.9	(2.71)	(1.37)[c]	blood orange
Complexes: Pd(II)$(4\text{-pyLOH})_2Cl_2$							
R = -phenyl	470	363	21.3	27.5	6.52	3.97	pale yellow
R = -4-methylphenyl	485	361	20.6	27.7	9.58	4.24	yellow-orange
R = -4-methoxyphenyl	492	353	20.3	28.3	8.03	3.11	blood orange

[a] These values are apparent ε's as this alcohol was not completely converted to carbenium ion in 70% $HClO_4$.

[b] The extremely limited solubility of this complex in 70% $HClO_4$ prevented any value from being obtained.

[c] These complexes were completely converted to carbenium ion in 70% $HClO_4$ but their limited solubility prevented reliable ε values from being determined.

this directly. This band is the so-called "x" electronic band so classified by Lewis and Calvin (60) in an elegant work on the color of organic compounds. Similarly, the higher energy, less intense (in this case) band, is labeled the "y" band (60). Certain relevant trends are established by the spectral position shifts of these main absorption bands which occur upon proceeding from R = phenyl to R = 4-methoxyphenyl (see Table II) for a related series of carbenium ions; and from the comparison of the spectrum of a free alcohol carbenium ion to that of the corresponding complexed carbenium ion. An inspection of the respective $\bar{\nu}_{max}$ values (Table II) reveals these trends to be the following:

(i) For carbenium ions derived from a family of precursors (e.g., the 2-pyridyl alcohols, the 4-pyridyl alcohols, etc.), in proceeding from R = phenyl to R = 4-methoxyphenyl $\bar{\nu}_{max}$ of the x-band decreases ca. 0.4 — 0.5 kK for the free alcohol ions and ca. 0.9 — 1.0 kK for the complexed alcohol ions. And for the 4-pyridyl ions the x-band $\bar{\nu}_{max}$ for a given free alcohol ion is lower than that for the corresponding complexed ion, with the difference in related x-band frequencies diminishing in going from R = phenyl to R = 4-methoxyphenyl. Thus, whereas the x-band $\bar{\nu}_{max}$ is at 20.7 kK (free alcohol ion) and 21.3 kK (bis-complexed ion) respectively for R = phenyl, it is at 20.2 kK (free alcohol ion) and 20.3 kK (complexed ion) for R = 4-methoxyphenyl.

(ii) Making the same comparisons as in (i) (above) on the relative y-band $\bar{\nu}_{max}$ values reveals that proceeding from R = phenyl to R = 4-methoxyphenyl results in a concomitant increase in $\bar{\nu}_{max}$ of ca. 0.7 kK; but this does not include the free 4-pyridyl ions where an increase in y-band $\bar{\nu}_{max}$ of only ca. 0.3 kK is encountered. And, in this case the

y-band $\bar{\nu}_{max}$ for a given 4-pyridyl ion is found to be higher (usually 0.7 - 1.0 kK) than the y-band $\bar{\nu}_{max}$ of the corresponding complexed ion. Here, however, no apparent trend exists in the magnitudes of observed difference in y-band $\bar{\nu}_{max}$ values for a related free ion — complexed ion pair.

(iii) A comparison of the x- and y-band $\bar{\nu}_{max}$ values of a free 2-pyridyl ion and corresponding 4-pyridyl ion shows that for a given R group $\bar{\nu}_{max}$ is always lower for both the x and y absorptions. (Note: This particular trend was also exhibited by a related series of 2-thiazolyl vs. 5-thiazolyl carbenium ions (8). That is, the x and y absorptions exhibited by a 2-thiazolyl ion were always found to be at lower $\bar{\nu}_{max}$ than the same absorptions for the corresponding 5-thiazolyl ion.)

For convenience and simplicity these spectral trends are summarized in the immediately succeeding statements. The effect of proceeding from R = phenyl to R = 4-methoxyphenyl is reflected by a bathochromic (red) shift of the x-band and an hypsochromic (blue) shift of the y-band. And, the effect of coordinating the carbenium ion always results in an hypsochromic x-band shift and a bathochromic y-band shift. It can now be shown that these results are qualitatively in accord with considerations made previously concerning the electronic spectra of arylcarbenium ions. For instance, if the energy of the x-band transition exhibited by pyridylcarbenium ions is dependent primarily upon a flow of electrons towards the exocyclic carbon atom from the aryl group(s) which are of predominant electron releasing capability, it is expected, and found, that the energy of this transition is reduced upon replacing R = phenyl with R = 4-methylphenyl, or R = 4-methoxyphenyl. The

subsequent cross-conjugational effect of this R substitution on the energy of the y-band transition is illustrated by the corresponding y-band blue shift in the spectra of a related series of ions. More important to this work, however, are the band shifts which take place as a consequence of complexation of a given carbenium ion. It follows that if the transition energy of either or both of the bands (x, and or, y) in the spectrum of a pyridylcarbenium ion is associated, at least to a degree, with a flow of electrons from the pyridine ring to the exocyclic carbon atom, any change in the electronic nature of the pyridine ring making it a more effective electron releasing moiety should result in a lowering in energy of that (those) electronic band(s). Furthermore, it is reasonable to expect that the coordinated pyridine ring would in fact be a better donor than the pyridine ring in the uncomplexed ion as in 70% $HClO_4$ the ring nitrogen is certainly protonated in the free ion, vide infra. Clearly then, any difference in these situations should reside in the fact that in the coordinated pyridine case electrons flow from an ostensibly neutral ring towards the exocyclic carbon; whereas in the uncoordinated pyridine carbenium ion electrons are required to flow from a ring which already bears a positive charge (the proton) resulting in a comparably unfavorable energetic transformation. Now, since coordination of a given pyridylcarbenium ion results in a blue shift of the x-band, and a relatively substantial red shift of the y-band, it appears to be the case that the y-band transition energy is, to an appreciable degree, paronymously related to the pyridine ring, and therefore dependent upon its electronic nature. These arguments, of course, serve to indicate that the pyridine ring is the so-called aryl" which appeared in the wave equation, $\psi_I = \{5\}$,

and $\psi_{II'}$, = {7}, presented previously (p. 70). So, from a qualitative standpoint it is reasonable that the π-electron energy level of $\psi_{II'}$ would be lowered with the pyridine ring protonated relative to the energy level of ψ_{II}, with this ring coordinated, as in the protonated situation the pyridine ring would be expectedly more electronegative. Hence, if the energy level of ψ_I is not altered as much as that of $\psi_{II'}$ for each of these two possibilities, the y-band should (and does) shift red for the coordinated carbenium ion relative to the "free" ion. It is also suggested that these assessments are correct owing to the magnitude of shift in energy observed for the y-band upon pyridylcarbenium ion coordination. An inspection of the $\bar{\nu}$ data (Table II, pp. 77-78) for the 4-pyridyl ions reveals that coordination induces a red shift in the energy of the y-band proportional to as much as 2.1 kK for the palladium complexes of the R = 4-methylphenyl ion vs. the corresponding "free" ion. Similarly, for this ion, the x-band is blue shifted only 0.4 kK. (This trend is also realized by the remainder of the data found in Table II. Furthermore, related data reported previously by Richardson (6) and by Wentz (8) support this trend.) Consequently, the electronic energy changes which are produced in the ion via coordination appear to be related principally to the attendant changes in the transition energy of the y-band. This engenders the speculation that relative energetic contributions provided by coordinated metal species towards stabilizing "complexable" carbenium ions would be reflected in a comparison of the respective y-band transition energies for a given complexed ion. Perhaps future work will furnish this possibility with substance.

Carbenium Ion Stability in $HClO_4 - H_2O$ as Determined by the "Deno" Titration Method. The suitability of the Deno titration method (10,11) for the determination of the thermodynamic stabilities of the carbenium ions investigated in this study has been aptly demonstrated by Wentz (8). The interested reader is referred to this work for a salient discussion of the necessary and pertinent experimental considerations. Reagent perchloric acid, 70% $HClO_4$, has proved to be a most appropriate ionization medium for these titrimetric stability determinations. It is a potent mineral acid as reflected by its thermodynamic ionization constant (K_{HClO_4}) reported to be 3800 (61). In fact, as pointed out by Gillespie (62), $HClO_4 - H_2O$ systems can be more acidic than reagent H_2SO_4, and only certain, nonaqueous superacid systems afford higher acidity than aqueous $HClO_4$. Indeed, $HClO_4 - H_2O$ is found to be uniquely between neat H_2SO_4 and superacid systems such as $HSO_3F - SbF_5$ (used by Olah (63) to prepare many relatively unstable carbenium ions) as a useful solvent for the generation of trityl-type carbenium ions. Freedman (64:1535) has commented that carbenium ion investigations in concentrated H_2SO_4 can be complicated by side reactions such as sulfonation or oxidation which in turn can destroy either the parent carbinol or the carbenium ion. Problems such as these are without a doubt responsible for much of the confusion found present in carlier studies on carbenium ions. The superacid system $HSO_3F - SbF_5$ as well, recently has been shown to generate carbenium ions as a consequence of oxidation by SbF_5 or SO_3 (65). Thus, previously devised methods and mechanisms of carbenium ion generation in this solvent may require extensive modifications. Furthermore, the use of superacids for the preparation of these types of carbenium ions would certainly require modifications of the

Dano titration method to take into account the fact that superacid media are nonaqueous. Therefore, at the minimum, the definition of new acidity function parameters would be requisite, as well as drastic alterations of the mechanics of the aqueous titration technique.

A consideration of the equilibria which pertain upon carbenium ion generation is in order. An examination of the literature in this area reveals that on occasion various authors are wont to write H^+ as the acid species responsible for the conversion of carbinol to carbenium ion. Albeit convenient, this practice is certainly not rigorous, and can frequently be misleading. In the present situation where perchloric acid has been employed as the ionizing medium it is necessary to choose between $HClO_4$ or H_3O^+ as the principal proton source towards the ion precursor carbinols, assuming, of course, that other complex or unusual acid species do not exist in this system in appreciable concentration. Since concentrated solutions of such mineral acids as H_2SO_4, HNO_3, or HCl, are not capable of carbenium ion generation in instances where $HClO_4 - H_2O$ is, it follows that $HClO_4$ is the acid species responsible for carbenium ion formation in those systems in which these other acids produce little or no carbenium ion. As a result of nmr studies on $HClO_4 - H_2O$, Redlich and Hood (66) reported that reagent 70-72% $HClO_4$ (ca. 11.8 M) is approximately 75% ionized. Hence, sufficient molecular $HClO_4$ is present in 70% $HClO_4 - H_2O$ for carbenium ion generation in systems which contain as solute limited quantities of ion precursor pyridylmethanol. And here, concentrated solutions of H_3O^+ do not convert carbinol to carbenium ion to any appreciable extent, except for the relatively more stable cations such as those which contain strongly electron releasing phenyl ring substituents such as 4-methoxy

groups. Thus, the ionization of triphenylcarbinol in $HClO_4 - H_2O$ may be written appropriately as:

$$(C_6H_5)_3COH + 2\ HClO_4 \rightarrow (C_6H_5)C^+ + H_3O^+ + 2\ ClO_4^- \qquad \{8\}$$

And, even though ring nitrogen protonation of the free alcohol ions tends to complicate the attendant equilibria, the pyridylmethanols should be ionized similarly. (Also, see the discussion which ensues (p. 98) in reference to the stability data contained in Table V.)

The equation for the Deno acidity function (H_R) may be written as

$$H_R = pK_{R^+} + \log \frac{[R\text{-}OH]}{[R^+]} \qquad \{9\}$$

where the values of H_R for a particular acid medium are a measure of the capability of that medium at various concentrations to ionize a given alcohol (R-OH) generating the corresponding carbenium ion (R^+). Since this equation is of the form, $y = b + mx$, it follows that if a series of values for H_R are known, and if the respective concentrations of R-OH and R^+ for a related alcohol — carbenium ion pair can be experimentally determined at the different H_R's, pK_{R^+} may be obtained as a quantitative measure of the thermodynamic stability of a given carbenium ion. Of course, it is required therefore that the acid medium be capable of measurably ionizing the alcohol over a range of acid concentrations; and it is also inherently required that in order for the H_R relationship to hold, the slope (m) of the curve got by plotting H_R vs. the log term be equal to 1.00. Wentz (8) showed that both of

these conditions were met in $HClO_4 - H_2O$ for the pyridylmethanols which are considered in this work.

A list of H_R values for aqueous $HClO_4$ and the corresponding wt % acid are given in Table III, p. 87. A plot of $-H_R$ vs. wt % acid (Figure 9, p. 88) yielded a smooth curve of approximately constant slope which was easily extrapolated (as shown in Figure 9) to 70.0% $HClO_4$ in order to obtain H_R values for acid concentrations greater than 60.0%. Employment of the fact that Beer's law ($A = \varepsilon cb$) directly relates the absorbance (A) of an absorbing species to its molar concentration (c), allows values for $[R\text{-}OH]/[R^+]$ in equation {9} to be obtained by measuring the absorbance (to ±0.001 absorbance units) of the carbenium ion at various $HClO_4$ concentrations. The absorbance (concentration) of R-OH was then taken as the difference between the Beer's law absorbance of the carbenium ion (see Dilution Curves, p. 93) and the actual absorbance of the ion at a given acid concentration. This method of data treatment is valid since R-OH does not absorb at λ_{max} of the carbenium ion. Consequently, it is justifiable to assume that when the actual absorbance of the carbenium ion matched the expected absorbance as predicted from Beer's law, the alcohol was ionized to an extent of ca. 100%. Naturally then, as the ionizing acid was systematically diluted (actually, at the onset of the titration molecular $HClO_4$ is also converted to H_3O^+, ClO_4^-) by the addition of measured increments of water, the absorbance fall off was linear (Beer's law dependent) as long as the alcohol remained essentially 100% ionized. However, as soon as the carbenium ion became titrimetrically reconverted to alcohol precursor as a result of further addition of water, absorbance fall off was no longer linear; and indeed, it was greater than that predicted

Table III
Values of H_R in Aqueous $HClO_4$ at 25°

$-H_R$	Wt % $HClO_4$[a]
3.79	30.0
4.61	35.0
5.54	40.0
5.95	42.0
6.38	44.0
6.82	46.0
7.31	48.0
7.86	50.0
8.45	52.0
9.05	54.0
9.68	56.0
10.37	58.0
11.14	60.0

[a]Deno et al. (11)

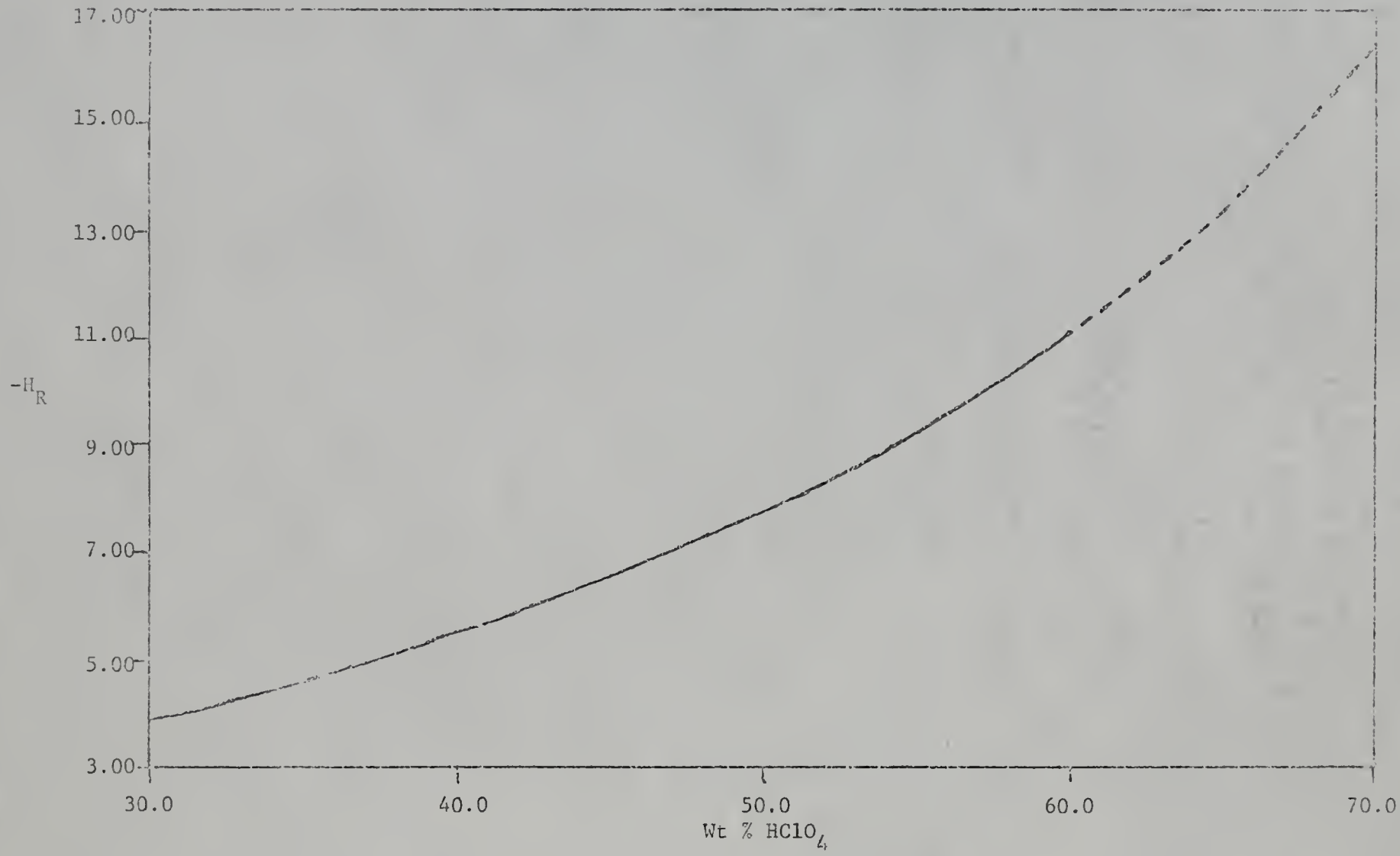


Fig. 9. Values of H_R in aqueous $HClO_4$ at 25°

from an extrapolated Beer's law straight line. An examination of the dilution curves (Figures 10-12, p. 93) illustrates this straightforwardly. Thus, for each carbenium ion so titrated, a collection of absorbance data was obtained as a function of changing wt % $HClO_4$.

Data treatment was carried out using the methods employed by Wentz (8) with some minor modifications. These methods may be described conveniently in conjunction with a stepwise examination of the pertinent arithmetic relationships required for data treatment. Initially, an unweighed sample of ion precursor pyridylmethanol (free or complexed) is dissolved in sufficient reagent $HClO_4$ (determined as 70.87%, see below) to produce an acceptable on-scale (viz., 15-25% T) spectrophotometer reading at λ_{max} for the absorbing species (the carbenium ion). The total solution sample is now weighed and the absorbance recorded. Then, measured increments of deionized water are added to the carbenium ion solution and, after thorough mixing, the absorbance of the sample is reread. The wt % of the acid solvent resulting from dilution is calculated from:

$$\text{Wt \% acid} = \frac{\text{wt (g) of acid}}{\text{wt (g) of sample} + \text{st (g) of } H_2O \text{ added}} \qquad \{10\}$$

where wt of acid = original wt % acid (70.87%) x original total sample wt. Thus, the wt % of the acid can be determined following each dilution by simply noting the cumulative quantity of water which has been added to that stage in the titration. The volume of the sample following each addition of water is then determined from:

$$\text{Sample volume (ml)} = \frac{\text{cumulative sample wt (g)}}{\text{corresponding } \rho \text{ (g/ml) of the sample}} \quad \{11\}$$

where ρ = specific gravity of the acid solvent. And therefore, it is obviously necessary to have values of ρ for aqueous $HClO_4$. (Wentz had obtained this information from a plot of ρ (4 sig. fig.) vs. wt % (4 sig. fig.) for solutions of aqueous $HClO_4$ (see Table IV, p. 91).) However, since the volume of an aqueous $HClO_4$ solution does not increase linearly upon dilution with water (i.e., the volumes of water and parent acid solution are not additive), Wentz found it necessary to "blow up" this plot in the region of each wt % datum point in order to obtain the corresponding value for ρ. This procedure was found to be extremely tedious owing to the difficulty found in obtaining 4 sig. fig. accuracy (to insure reliability of related data to 3 sig. fig.) for a considerable amount of wt % data from such a graphical readout. This particular problem was conveniently alleviated by taking a "least squares" curve fit of Brickwedde's data (67), (Table IV, p. 91) to yield a "printed out" series of values for ρ spanning the range 0.00 wt % $HClO_4$ to 75.00 wt % $HClO_4$. (The details of this least squares treatment are given in the Appendix.) Thus, having experimentally determined ρ of the original reagent acid, the corresponding wt % of the original acid was obtained from this ρ — wt % tabulation. The use of equation {10} then yielded wt % data for subsequent dilutions, in turn for which corresponding ρ values were available from the ρ — wt % tabulation. Finally, it is necessary to determine the dilution fraction (D.F.) for each dilution. This is obtained from:

Table IV
Specific Gravity of Aqueous $HClO_4$ Solutions at 25°

Specific Gravity (g/ml)	Wt % $HClO_4$[a]
0.997	0.00
1.026	5.00
1.056	10.00
1.088	15.00
1.123	20.00
1.160	25.00
1.200	30.00
1.244	35.00
1.291	40.00
1.343	45.00
1.400	50.00
1.462	55.00
1.527	60.00
1.596	65.00
1.664	70.00

[a]Brickwedde (67)

$$D.F. = \frac{\text{original sample volume (ml)}}{\text{cumulative sample volume (ml)}} \qquad \{12\}$$

Again, inspection of equation {9} reveals that the required values for the log term are ratios of concentrations (of alcohol to corresponding carbenium ion), and not absolute concentration values. Thus, it is not necessary to determine the concentration of the absorbing species at any time during the titration. It is only necessary to measure absorbances throughout the titration at the various, known dilution fractions, which are proportional to changes in the concentration of the absorbing species. Hence, a plot of absorbance (A) vs. dilution fraction (D.F.) yields a plot which reflects the decrease in concentration of carbenium ion as a consequence of dilution as well as of reconversion to alcohol precursor. And, the only requirement which must be met in order for this treatment to hold is that the alcohol be ionized completely at the onset of the titration. An examination of the dilution curves for free and complexed carbenium ions derived from the same alcohol precursors (Figures 10-12, p. 93) clarifies these considerations. In each case the beginning of the titration (i.e., in the vicinity of D.F. = 1.00) corresponds to a linear fall off of absorbance with dilution. Thus, at this juncture of the titration the alcohol precursor species is essentially completely ionized; and, to repeat, the effect of the addition of titrant (water) is to titrate molecular $HClO_4$ while only diluting the carbenium ion. When the equilibrium reconversion of carbenium ion to alcohol (described by equation {1}, p. 9) becomes measurable the titration curve begins to slope down and away from the extrapolated Beer's law straight line as seen in the dilution curves.

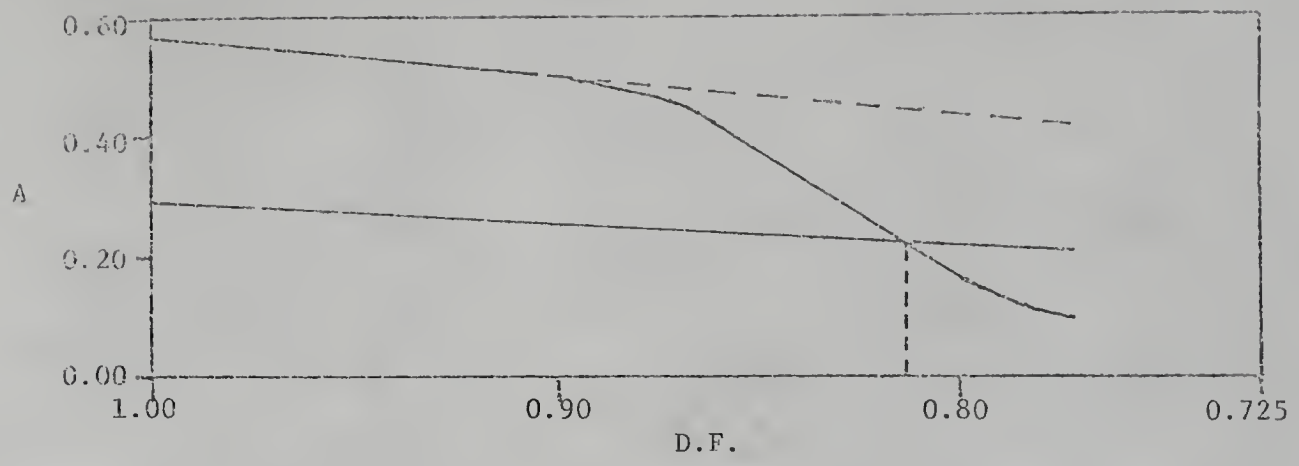


Fig. 10. Dilution curve for the titration of 4-pyridyl-4-methylphenyl-4-fluorophenylcarbenium ion

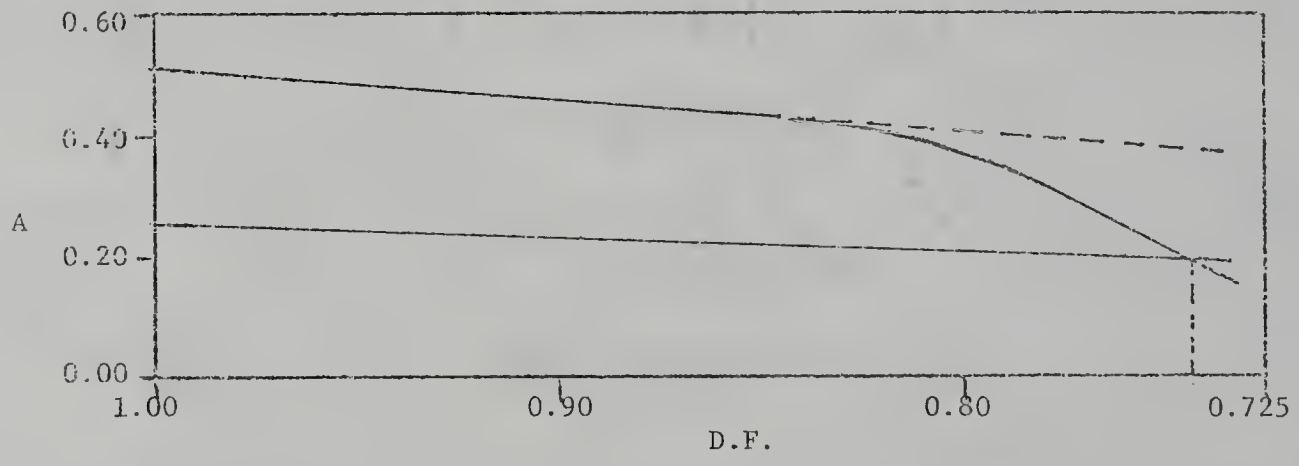


Fig. 11. Dilution curve for the titration of $[Pd(II)(4\text{-pyL})(L_N)Cl_2]^+$, where 4-pyL = 4-pyridyl-4-methylphenyl-4-fluorophenylcarbenium ion

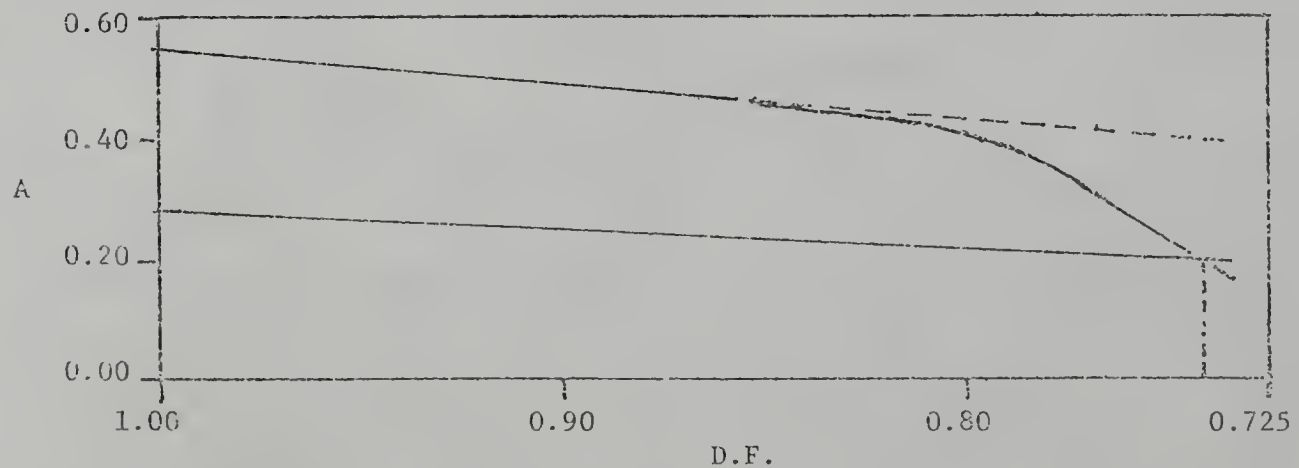


Fig. 12. Dilution curve for the titration of $[Pd(II)(4\text{-pyL})_2Cl_2]^{2+}$, where 4-pyL = 4-pyridyl-4-methylphenyl-4-fluorophenylcarbenium ion

The lower straight line shown (which practically bisects the plot horizontally) corresponds to the so-called "1/2" Beer's law line. This second line has been drawn by considering that if at the onset of the titration the concentration of the absorbing species (the carbenium ion only) were divided by two, its absorbance would also be divided by two. Thus, this "1/2" Beer's law line may be constructed from a series of points got by halving the absorbance values which served to establish the initial (upper) Beer's law line. Consequently, the intersection of this second Beer's law line with the dilution curve for a given carbenium ion marks the D.F. location at which [R-OH] is expected to equal $[R^+]$ during the titration of that ionic species. The point of this graphical treatment resides in the fact that the log term in equation {9} is equal to zero for equal values of [R-OH] and $[R^+]$. Hence, vertical extrapolation from this intersection point to the abscissa of the plot yields the D.F. at which the corresponding value of H_R equals pK_{R+} of that carbenium ion. Of course, H_R is obtained after relating D.F. to the appropriate wt % $HClO_4$, (note: here, simple arithmetic interpolation is usually necessary to obtain the required values for wt % $HClO_4$ since the data points used to plot the dilution curve seldom include the exact D.F. values at which [R-OH] = $[R^+]$), which in turn is related to H_R (see Figure 9, p. 88).

The thermodynamic stability data resulting from these titrimetric measurements upon the pyridylcarbenium ions investigated in this study are presented in Table V, pp. 95-96. The following considerations which are in respect to this data are relevant.

The reliability of the data was corroborated through a titrimetric measurement of pK_{R+} for triphenylcarbenium ion. The value obtained

Table V

Thermodynamic Stability Data Resulting from the "Deno" Titration of the Various Pyridylcarbenium Ion Species, in $HClO_4 - H_2O$ at 25°

Carbenium Ion Precursor	$K_{H^+pyL^+}$ [a]	pK	$\Delta G°$ (kcal mol^{-1})	$\Delta G°$ (kJ mol^{-1})
Alcohol: triphenylmethanol	1.7×10^{-7} [b]	6.76[b]	9.21	38.53
Alcohols: 2-pyLOH = 2-pyridyl-R-4-fluorophenyl-methanol				
R = -phenyl[c,d]	2.1×10^{-16}	15.68	21.36	89.37
R = -4-methylphenyl	2.1×10^{-14}	13.67	18.62	77.91
R = -4-methoxyphenyl	5.1×10^{-11}	10.29	14.01	58.62
Alcohols: 4-pyLOH = 4-pyridyl-R-4-fluorophenyl-methanol				
R = -phenyl[d]	3.4×10^{-14}	13.47	18.35	76.78
R = -4-methylphenyl	2.2×10^{-12}	11.66	15.88	66.44
R = -4-methoxyphenyl	1.0×10^{-9}	9.00	12.26	51.30

Table V — Extended

Carbenium Ion Precursor		pK	$\Delta G°$ (kcal mol^{-1})	$\Delta G°$ (kJ mol^{-1})
Complexes: Pd(II)(4-pyLOH)-$(L_N)Cl_2$	$K_{[Pd(II)(4\text{-}pyL)(L_N)Cl_2]^+}$ [e]			
R = -phenyl[d]	2.0×10^{-12}	11.70	15.94	66.69
R = -4-methylphenyl	2.6×10^{-11}	10.58	14.41	60.29
R = -4-methoxyphenyl	1.5×10^{-8}	7.82	10.65	44.56
Complexes: $Pd(II)(4\text{-}pyLOH)_2$-Cl_2	$K_{[Pd(II)(4\text{-}pyL)_2Cl_2]^{2+}}$ [e]			
R = -phenyl[d]	6.2×10^{-13}	12.21	16.63	69.58
R = -4-methylphenyl	2.7×10^{-11}	10.57	14.40	60.25
R = -4-methoxyphenyl	1.2×10^{-8}	7.93	10.80	45.19

[a] $K_{H^+pyL^+}$ is the stability constant for a "free" alcohol carbenium ion.

[b] Compare to $K_{R^+} = 1.4 \times 10^{-7}$, $pK_{R^+} = 6.89$, $\Delta G° = 9.37$ kcal mol^{-1}; for R^+ = triphenylcarbenium ion; Deno et al. (11).

[c] Stability data for this alcohol were not obtainable by the "Deno" titration method. The values provided follow from ^{19}F nmr studies and appropriate LFE relationships (p. 119).

[d] See the discussion (pp. 103-106) concerning rearrangement of the carbenium ions derived from these alcohols and the complexes thereof.

[e] These are the stability constants for the "mono" and "bis" complexed carbenium ions.

(Table V) is in good agreement with pK_{R+} measured for this ion in 60% $HClO_4$ by Deno and coworkers (11) using the titration technique.

A requirement which obviously must be met by the complexed carbenium ions to insure that the corresponding stability data be meaningful is that the coordinate bond between the palladium metal center and the pyridine ring remains intact throughout titration. Undoubtedly, the protonic solvent will compete strongly for the basic ring nitrogen site(s) as evidenced by the fact that the pyridine ring is protonated for the "free" alcohol ions in 70% $HClO_4$ (shown below). The simplest demonstration of the stability of the coordinate bond during titrimetric (and ^{19}F nmr chemical shift) measurements stems from the fact that the electronic spectrum of a given complexed 4-pyridylcarbenium ion in $HClO_4 - H_2O$ remains unchanged for a period of at least a few hours. In fact, the electronic spectrum of the bis complex of 4-pyridyl-4-methylphenyl-4-fluorophenylcarbenium ion in $HClO_4 - H_2O$ was found to remain intact for 12 hours as evidenced by the fact that during this time no appreciable change in band intensity could be observed; and, more importantly absolutely no shifts of the x- and y-absorption bands had taken place. Furthermore, the solution color of the complexed ion did not deteriorate to the solution color of the corresponding "free" ion. Additional investigations on the intact nature of complexed carbenium ion electronic spectrum in $HClO_4 - H_2O$ upon the lone 2-pyridylmethanol complex isolated (see Experimental, p. 36) revealed that as soon as this compound was dissolved in the acid the intensities of the x- and y-absorptions began to increase steadily; and also, the x- and y-absorptions began to shift immediately towards the respective positions of these absorptions characteristic of the uncoordinated, "free" 2-pyridylcarbenium ion.

Thus, this 2-pyridylcarbenium ion complex was insufficiently stable to be studied using $HClO_4 - H_2O$ as an ionizing medium. A comparison of the stability data for a related free ion — complexed ion series also serves to establish that the metal — nitrogen bond(s) remain(s) intact during thermodynamic measurements, and that coordination certainly stabilizes a given carbenium ion relative to the corresponding free ion. An examination of the respective ΔG° values (Table V) indicates that the degree of stabilization afforded by coordination is greatest for the 4-pyridylphenylcarbenium ion. Although the thermodynamic titration data for the unsubstituted phenyl carbenium ions is somewhat suspect owing to rearrangement of these ions in $HClO_4 - H_2O$ (discussed, pp. 103-106), ^{19}F nmr chemical shift measurements in conjunction with relevant free energy relationships substantiate the reliability of the reported stability data, vide infra. The stabilizing influence of coordination upon a given carbenium ion is also seen on inspection of the dilution curves for a free ion — complexed ion related series (see Figures 10-12, p. 93). Here, the Beer's law dependence of the plot reflects the relative stability of a given carbenium ion. That is, a relative comparison of the D.F. values corresponding to that point in the titration at which each dilution curve no longer adheres to Beer's law, allows an ordering of the stability of all carbenium ions investigated by the titration method. This particular D.F. for the free 4-pyridyl-4-methylphenyl-4-fluorophenylcarbenium ion is ca. 0.92, whereas the corresponding D.F. values for the complexes of this ion are ca. 0.87, thereby showing that the coordinated ions are more stable.

The stability constant values (K) found in Table V correspond to the equilibria which are established upon the titrimetric reconversion

of a particular pyridylcarbenium ion to its free or complexed precursor. The equations for these equilibria have been presented previously (p. 16) but for expedient purposes they are repeated in the order in which they are discussed. The equilibrium titration of a free alcohol ion is represented by:

$$H^{+}pyL^{+} + 2\ H_2O \rightleftarrows H^{+}pyLOH + H_3O^{+} \qquad \{2\}$$

This statement is consistent with the fact that the unionized alcohol is protonated. This is certainly expected for pyridine in such strongly acidic media as 45-70% $HClO_4$ (these values correspond to the acid concentration ranges spanned during the titration of the more stable carbenium ions). Moreover, Wentz (8) demonstrated that equation {2} was the correct equilibrium statement for describing the titrimetric reconversion of an uncoordinated thiazolylcarbenium ion to its alcoholic precursor. This was accomplished by titrating the N-methyl iodide salt of a particular 2,4-dimethyl-5-thiazolylcarbenium ion yielding a K value which was identical to that which he had obtained for the titration of the original alcohol ion. Clearly then, in each instance the thiazole ring nitrogen must have borne a unit positive charge throughout titration. Also, by assuming that the pyridylmethanol pyridine ring is of similar basicity as pyridine itself (K_b pyridine = 2.3×10^{-9}), it can be shown from simple acid-base equilibria that a given pyridylmethanol dissolved in 1 M H_3O^{+} at an initial alcohol concentration of 0.01 M, is protonated to an extent in excess of 99.99%! (This calculation is given in the Appendix.) Since, for the $HClO_4 - H_2O$ — pyridylmethanol systems considered, the combined concentration of $HClO_4 - H_3O^{+}$

is always much greater than 1 M, and the concentration of a pyridylmethanol is very small comparatively, the pyridine nitrogen is protonated (ca. 100%) for a free alcohol carbenium ion. A direct effect of ring nitrogen protonation on carbenium ion stability is indicated from a comparison of the data in Table V for a structurally related pair of free 2- and 4-pyridylcarbenium ions. That is, a 2-pyridyl ion is seen to be considerably less stable than its 4-pyridyl congener. The only significant difference between such a related pair of cations should reside in the disproportionate degree of positive charge separation in the 2-pyridyl vs. the 4-pyridyl ion. Hence, it appears that the destabilizing consequence of like-charge repulsion on the stability of a given 2-pyridylcarbenium ion is relatively substantial in that the positive charge on the 2-pyridyl nitrogen is in much closer proximity to the carbenium ion center than in the corresponding 4-pyridyl ion situation.

The equilibrium titrations of the coordinated carbenium ions may be represented by:

$$Cl_2(L_N)Pd(II)pyL^+ + 2\,H_2O \rightleftarrows Cl_2(L_N)Pd(II)pyLOH + H_3O^+ \qquad \{3\}$$

and

$$Cl_2Pd(II)(pyL)_2^{2+} + 4\,H_2O \rightleftarrows Cl_2Pd(II)(pyLOH)_2 + 2\,H_3O^+ \qquad \{4\}$$

Statement {3} designates the reconversion of a singly charged coordinated carbenium ion to its complexed "mono" alcohol precursor. The stability data associated with this transformation therefore afford a reflection

of the stabilizing effect exerted by the metal on a single pyridylcarbenium ion. Statement (4) corresponds to the reconversion of a "bis" carbenium ion complex to its alcoholic precursor and is premised upon complete ionization of both of the coordinated alcohols in 70% $HClO_4$ (i.e., prior to titration). The ε data (Table II, pp. 77-78) indicate that both coordinated alcohols are ionized for the bis complexes in the acid. The ^{19}F nmr chemical shift data (vide infra) also corroborate this consideration stemming from the fact that the absorption position of the ^{19}F nmr signal for a mono complexed ion is identical to that found for the corresponding bis complexed ion. If both the coordinated alcohols in the bis complex were not ionized, either a time averaged signal would be expected or two signals would be observed in the spectrum corresponding respectively to an ionized and an unionized ligand molecule. That is, the ^{19}F nmr spectrum should reflect the presence of either two rapidly equilibrating, or two distinctly different, fluorine nuclei. Furthermore, as previously indicated, the dilution curves resulting from the titrations of the bis complexed ions all exhibit appreciable Beer's law dependency at the onset of the titration. If the bis complexes had not been ionized completely upon dissolution in 70% $HClO_4$, an immediately detectable equilibrium would have been established upon addition of the initial quantities of titrant (water), and no Beer's law dependence would have been illustrated by the Beer's law plot at the beginning of the titration. This consideration alone does not preclude the unique possibility of having ionized only one of the coordinated alcohols in a bis complex in 70% $HClO_4$. However, the ε data, which indicate multiple ionization of the bis complexes in the acid, provide rather forcing evidence substantiating the assertion that both

of the coordinated alcohols are converted to carbenium ion in 70% $HClO_4$. Indeed, as the bis complexes dissociate in the acid, no increase in absorption intensity is detectable. Thus, both coordinated alcohols must have been ionized. Of course, this contention could be definitively established by titrating a weighed sample of a bis complex *vs.* the corresponding mono complex, for which twice the quantity of water would be required to reconvert the bis complexed ions to the neutral precursor if both coordinated alcohols had been ionized initially.

It is also pointed out that the values for the thermodynamic data in Table V correspond to the reverse of the titration equilibria (equations {2}, {3}, and {4}) as written. Hence, an examination of these data in relation to the relative ease of carbenium ion formation affords a measure of the stability (as opposed to instability) of that ion. In writing these equilibria it was tempting to consider the equations which obtain upon carbenium ion generation; *viz.*, for a free alcohol ion:

$$H^+pyLOH + 2\ HClO_4 \rightarrow H^+pyL^+ + H_3O^+ + ClO_4^- \qquad \{13\}$$

That is, this statement illustrates the net chemical change which occurs upon dissolving a protonated pyridylmethanol in 70% $HClO_4$ and obviously corresponds to carbenium ion formation. (It is not germane to consider the proton source required for the initial protonation of the pyridine ring.) It must be emphasized, however, that the carbenium ion stability data were obtained from the aqueous titrations which are correctly described by equations {2}, {3}, and {4}; and it is for this reason that this distinction has been made.

Finally, a comparison of the stability data for the mono complexes to the data for the corresponding bis complexes proves worthwhile. These data suggest that related mono -- bis complexed carbenium ions are of practically identical thermodynamic stability. In the absence of charge effects this would have been an expected result. However, based upon the consequence of like-charge repulsions on the stabilities of related free 2-pyridyl *vs.* 4-pyridylcarbenium ions, it seems reasonable that a given bis complexed ion would be somewhat less stable than the corresponding mono complexed ion. Apparently, therefore, the degree of charge separation in the bis complex "di"-carbenium ion is sufficiently great that there is no residual ion destabilizing effect exerted mutually upon one another by the two coordinated ions in the complex. This stability similarity is also reflected by a virtual superimposability of the dilution curves for a related pair of these complexed carbenium ions. Thus, the stabilizing influence exerted by the metal center on the stability of such 4-pyridyl complexed ions appears to be independent of mono *vs.* bis coordination. Although, it may be the case that destabilization arising through charge repulsions in the bis ions is counterbalanced by enhanced stabilization through solvation in the highly polar $HClO_4 - H_2O$ solvent system. This possibility is suggested as a consequence of the considerably greater solubility of the bis *vs.* the mono complexes in $HClO_4 - H_2O$. Additional studies are required to test and confirm the validity of this explanation.

The Problem of Carbenium Ion Rearrangement in $HClO_4 - H_2O$. Initial attempts to gather stability information for the carbenium ions derived from the free and complexed unsubstituted phenyl pyridylmethanols led

to rather unusual and unanticipated results. For instance, it was discovered that the dilution curves for the $HClO_4 - H_2O$ titrations of these carbenium ions could not be treated by the "1/2" Beer's law line extrapolation technique in order to get the corresponding stability constant data! That is, the second portion of the dilution curves (cf., Figures 10-12) obtained for any of these particular ions never fell off sufficiently to intersect with the "1/2" Beer's law line. In other words, the intensities of the principal electronic absorptions of these ionic species were found to grow steadily on standing (until the intensities had magnified by a factor of ca. 1.5 of original). In relation to this unanticipated result was the fact that the ^{19}F nmr signal initially exhibited by $HClO_4 - H_2O$ solutions of these ions was found to disappear with time (ca. within 1-2 hours to 24 hours depending upon the original concentration of the carbenium ion under investigation). The nmr result suggested therefore that the para-fluorine phenyl ring substituent was discharged kinetically. Shutske's results (68) verified this contention. Shutske studied the reduction of various fluorospiro(isobenzofuran-piperidine)s in 97% formic acid and discovered that on standing fluorine was lost as a phenyl ring substituent in the parent compound. This result prompted Shutske to repeat the investigations of Dayal et al. (69) on the reduction of 4-fluorophenyldiphenylmethanol in 97% formic acid — sodium formate solution. Shutske recognized the similarity of this investigation to the fluorospiro study with respect to the anticipated ejection of the para-fluorine substituent. Dayal et al. had reported the isolation of only 4-fluorophenyldiphenylmethane as the reduction product. Shutske, however, found that although this alkane was the principal reduction product, 4-hydroxydiphenylmethane was also obtained

in a yield of 13%. Consequently, the loss of the para-fluorine substituent from the unsubstituted phenyl pyridylmethanols in $HClO_4 - H_2O$ paralleled Shutske's results. And, in retrospect, this result indicates that the ability of a 4-fluorophenyl group to participate in conjugational interaction with the exocyclic carbenium ion carbon via π--electron release is more substantial than is that of unsubstituted phenyl. This is, in fact, borne out by the results of various studies on the thermodynamic stabilities of trityl-type carbenium ions which also contain 4-fluorophenyl rings (18,19,70,71), etc. Hence, the degree of positive charge which migrates by resonance into the 4-fluorophenyl ring in these particular carbenium ions is significantly greater than for either of the ion systems containing 4-methylphenyl, or 4-methoxyphenyl substituted rings. Thus, in these latter cases the fluorine nucleus was not lost during studies on carbenium ions in $HClO_4 - H_2O$.

The "Deno" titration stability data (Table V) for the unsubstituted phenyl pyridylcarbenium ions were obtained in the following fashion. The initial portion of the dilution was plotted as usual (viz. absorbance vs. D.F.) to yield the Beer's law dependent region followed by the normal smooth curve deviation from the extrapolated Beer's law straight line. It can be seen by inspection of the dilution curves (Figures 10-12) that the plot is then again linear over a substantial region of the titration until a smooth curve upswing of the plot is reached which thereby establishes that the titration is virtually complete. That is, these curves are very similar to those got from ordinary acid — base titrations, with the difference that the pertinent carbenium ion equilibria persist over a rather substantial concentration range of the ionizing medium (ca. 10 wt % $HClO_4$), resulting in a titration curve

with considerably less drastic changes in slope than are customarily exhibited by acid — base titration curves. So, since the dilution curves for these carbenium ions (i.e., the ions which rearrange in $HClO_4 - H_2O$) exhibit curve upswing prior to intersection with the "1/2" Beer's law line, the so-called second straight line portion of the curve (that portion between curve downswing and curve upswing) was extrapolated to intersect with the "1/2" Beer's law line. This simple technique facilitated the isolation of the D.F. value for which [R-OH] = [R^+], and thereby allowed the determination of K_{R^+} for the unsubstituted phenyl carbenium ion in question. The reliability of the data obtained by this method was tested by precalculating appropriate wt %'s $HClO_4$ required to yield D.F. samples whose carbenium ion absorbance would tentatively lie on the extrapolated dilution curve in the region of interest. The D.F. samples tested in this fashion gave absorbances which coincided very well with absorbances predicted from the extrapolated plot. Hence, the stability data so obtained are considered to be very satisfactory. It will also be shown that ^{19}F nmr chemical shift data, in conjunction with attendant free energy relationships, serve to establish that these data are acceptable, vide infra. (Note: Certain experiments were performed in attempts to determine the nature of the species which resulted upon fluorine atom ejection. A brief account of this work is provided in the Appendix.) Furthermore, it is potentially of interest to study the stability of such fluorophenylpyridylcarbenium ions as a function of the rate of discharge of the fluorine substituent. Indeed, these experiments should be relatively straightforward to monitor via ^{19}F nmr, and could provide additional information concerning the carbenium ion stabilizing influence as exerted by various coordinated metals.

^{19}F Chemical Shifts and Carbenium Ion Stability. To repeat, the results of previous ^{19}F nmr investigations have demonstrated that a *para*-substituted fluorine nucleus on an aryl ring is a highly sensitive probe in regard to the stability of carbenium ions which are conjugated with the fluorine nucleus. Hence, further discussion respecting the appropriate nature of this nmr technique shall not be presented, excepting, of course, as it pertains to the ^{19}F nmr data obtained during the course of this work.

The use of ^{19}F nmr chemical shifts as a criterion for the stability of coordinated carbenium ions is, in itself, a novelty. Past studies which have employed ^{19}F nmr measurements for the purposes of elucidating the stability and structure of coordination compounds have normally incorporated fluorine into the system as a ligand itself, *i.e.*, fluoride ion (see, for instance, the nmr studies by Dixon and McFarland (72), and references to related work cited therein). Also, fluorine in this capacity has been used for nmr investigations as a substituent on a ligand moiety bound directly to the metal center such as in the controversial studies by Parshall (73,74). This author proportioned the measured ^{19}F chemical shift of 3- and 4-fluorophenyl groups coordinated to platinum(II) to the *trans*-directing abilities of ligands in the complex located *trans* to the fluorophenyl groups. In any event, it is believed that the current work embodies the first attempts to correlate ^{19}F chemical shifts with the thermodynamic stabilities of metal-complexed trityl-type carbenium ions.

The ^{19}F nmr spectra which were recorded for the free and complexed pyridylmethanol -- carbenium ions are uncomplicated and highly similar.

Each absorption pattern was characterized by the presence of a nontuplet fluorine signal which is predicted for $^{1}H - ^{19}F$ coupling in these systems by the relationship:

$$\text{Number of peaks} = (2\ I_1 n_1 + 1)(2\ I_2 n_2 + 1) \cdots (2\ I_n n_n + 1) \quad \{14\}$$

where $I_1 = I_2 = 1/2$ for hydrogen, and $n_1 = n_2 = 2$ for the two pairs of hydrogens situated ortho and meta respectively, to the single fluorine nucleus present in each species investigated. (The basic form of this equation is given in (75).) The center peak of the 9-fold absorption was expectedly the most intense. The only difference of consequence resulting from a comparison of all the spectra lies in the relative positions of the signals for each species. For simplicity, the center of the 9-fold resonance pattern is taken as the ^{19}F absorption position. Hence, the position of the fluorine signal, recorded relative to an appropriate reference standard, provides an indication of the stability of the carbenium ion under investigation relative to the degree of π-electron delocalization present within the structural framework of each carbenium ion species. The reference standards employed were external $CFCl_3$ and external trifluoroacetic acid (TFA). The use of two standards afforded a double check on the reliability of the obtained shift data. External referencing procedures were used for all carbenium ion spectra owing principally to the extremely reactive nature of the ion and of the $HClO_4 - H_2O$ solvent. Consequently, the absorption position of any internal standard might have been appreciably affected by interactions with solute, or solvent. Nonreactive, nonpolar materials, obviously could not be satisfactorily employed as internal references

because of their immiscibility with $HClO_4$ -- H_2O. Referencing against the same external standards also facilitated the comparison of chemical shift data obtained for the unionized ligands and complexes in acetone to the related data for the corresponding carbenium ions in $HClO_4$ — H_2O. Bulk susceptibility contributions by the solvent to carbenium ion chemical shifts were expected to be unimportant in that each ion spectrum was recorded in 70% $HClO_4$. Hence, solvent chemical shift susceptibility contributions were leveled for each nmr measurement.

The shift data resulting from these ^{19}F nmr investigations are given in Table VI, pp. 110-111. Since ^{1}H -- ^{19}F coupling is of no particular concern to this work, examples of the ^{19}F spectra are not given.) The following statements in relation to the relevant trends established by these data are in order. A comparison of δ values for the alcohols in acetone, 1 M $HClO_4$ and 70% $HClO_4$, systematically shows the effect of proceeding from an aprotic solvent, to a protonating solvent, to a solvent capable of carbenium ion generation. Consequently, a small downfield shift of the resonance for a given alcohol is detected upon protonation (i.e., acetone vs. 1 M $HClO_4$ as solvent); whereas transformation to carbenium ion is accompanied by a relatively substantial downfield shift in the ^{19}F signal. This same trend is exhibited by the complexes but, of course, no 1 M $HClO_4$ spectrum was recorded for these materials as they are not soluble at this acid concentration. Hence, as expected, conversion to carbenium ion results in appreciable resonance delocalization of positive charge throughout the conjugated molecular framework. In proceeding from R = -phenyl to R = -4-methoxyphenyl for any related series of carbenium ions an appreciable upfield shift of the ^{19}F signal is observed. This reflects the substantial capacity of

Table VI

^{19}F nmr Chemical Shifts (δ) for Carbenium Ion Precursors in Acetone and 1 M $HClO_4$, and for Carbenium Ions in 70% $HClO_4$ at 25°

Carbenium Ion Precursor	Solvent[a] / Ext. Standard: Acetone[b] / TFA	1 M $HClO_4$[c] / $CFCl_3$	1 M $HClO_4$[c] / TFA	70% $HClO_4$ / $CFCl_3$	70% $HClO_4$ / TFA
Alcohols: 2-pyLOH = 2-pyridyl-R-4-fluorophenylmethanol					
R = -phenyl	39.2	111.9	35.0	66.6	-10.2
R = 4-methylphenyl	39.4	111.9	35.1	75.5	-1.3
R = -4-methoxyphenyl	39.7	112.0	35.1	90.5	13.6
Alcohols: 4-pyLOH = 4-pyridyl-R-4-fluorophenylmethanol					
R = -phenyl	39.1	112.6	35.8	68.7	-8.1
R = -4-methylphenyl	39.2	112.8	35.9	77.3	0.4
R = -4-methoxyphenyl	39.4	112.7	35.8	91.5	14.8

Table VI -- Extended

Carbenium Ion Precursor	Solvent[a] Ext. Standard: Acetone[b] / TFA	1 M $HClO_4$[c] / $CFCl_3$	1 M $HClO_4$[c] / TFA	70% $HClO_4$ / $CFCl_3$	70% $HClO_4$ / TFA
Complexes: Pd(II)(4-pyLOH)(L_N)Cl_2					
R = -phenyl	38.6	-	-	[d]	[d]
R = -4-methylphenyl	38.6	-	-	80.4	3.5
R = -4-methoxyphenyl	38.7	-	-	92.5	15.6
Complexes: Pd(II)(4-pyLOH)$_2Cl_2$					
R = -phenyl	38.4	-	-	73.1	-3.8
R = -4-methylphenyl	38.6	-	-	80.4	3.5
R = -4-methoxyphenyl	38.6	-	-	92.4	15.5

[a] δ values are in parts per million(ppm), and are upfield relative to the external reference signal unless the value is negative, in which case δ is downfield relative to the external reference.

[b] Acetone solution spectra were recorded relative to external TFA only.

[c] δ values in these columns refer to the protonated alcohols.

[d] No ^{19}F carbenium ion signals were detectable for this species saturated in 70% $HClO_4$ following 5000 scans with the Fourier transform synthesizer.

a para-methoxyphenyl substituent relative to hydrogen, . . . and in turn relative to a para-fluorine substituent, to remove positive charge from the exocyclic carbon via conjugational interaction. A comparison of δ for the 2-pyridyl vs. the corresponding 4-pyridylcarbenium ions shows the destabilizing effect of like-charge repulsions on carbenium ion stability to be more significant in the 2-pyridylcarbenium ions. Hence, the ^{19}F signal for a given 2-pyridylcarbenium ion is downfield relative to its more stable 4-pyridylcarbenium ion congener. This is in keeping with the thermodynamic data which have been considered previously. The consequence of coordination on a given ^{19}F resonance is reflected by a substantial increase in δ found in proceeding from a free to the corresponding complexed ion(s). This trend also parallels related thermodynamic data obtained from the titrimetric investigations and again indicates that complexation stabilizes unsubstituted phenylcarbenium ions to the greatest extent.

For the data reported, it can be seen that the ^{19}F signals for a related mono- and bis-complexed carbenium ion pair are virtually identical. Since two ^{19}F resonances were not initially detectable for the bis complex ions, it is clear that both coordinated alcohols are converted to carbenium ion in 70% $HClO_4$; and again, a related mono- and bis-complexed carbenium ion pair are predicted to be of essentially equal thermodynamic stability. Here, it is conveniently pointed out that when the 70% $HClO_4$ ^{19}F nmr samples of the mono and bis complexes (of R = -4-methylphenyl, for example) were allowed to stand, eventually two signals developed. One of the signals coincided with the original coordinated carbenium ion absorption, whereas the newly developed signal coincided with the free carbenium ion resonance. These data verify the

intact nature of the coordinate bond between palladium and the pyridine ring in 70% $HClO_4$ as the second signal was not detectable within the first few hours of sample preparation. Furthermore, for the mono-complexed ion, the intensity of the free ion signal was not equal (approximately) in magnitude to that of the complexed ion until the sample had stood ca. 24 hours. Again, this demonstrates the stability of the coordinate bond.

The ^{19}F nmr shift data reported for the carbenium ions derived from the free and complexed unsubstituted phenyl pyridylmethanols are considered to be reliable for the following reasons. Principally, the detection of a ^{19}F signal in these systems for a freshly prepared sample essentially guaranteed that the nmr measurement was made on the species of interest. This follows since the originally detectable ^{19}F signal disappears only after rearrangement of these carbenium ions takes place. Free energy correlations (considered in the forthcoming section) also served to corroborate the credibility of the nmr data; and, as well, instated the use of appropriate ^{19}F chemical shifts for the determination of the thermodynamic stability of 2-pyridylphenyl-4-fluorophenylcarbenium ion (recall that the stability of this carbenium ion species was not titrimetrically measurable). As this particular carbenium ion was allowed to stand, several poorly resolved signals developed in the ^{19}F spectrum. An attempt was made to fingerprint these absorptions via comparison with the ^{19}F nmr spectrum of 1:5 48% HF – 70% $HClO_4$. The ^{19}F signal for HF in 96% H_2SO_4 reportedly exists at -116.9 ppm relative to external TFA (76), but no similar absorption was detectable in the HF – $HClO_4$ spectrum. Presumably, the HF reacted with the glass nmr tube to produce silicon fluorides or fluorosilicates.

Similar side products were expected for the remaining unsubstituted phenylcarbenium ion samples where HF was also the initially anticipated fluorine containing rearrangement product. A comparison of all unsubstituted phenylcarbenium ion nmr spectra, however, yielded little correspondence of resonance positions for the signals which developed upon rearrangement. (For the concerned reader: the 2-pyridylphenyl-4-fluorophenylcarbenium ion spectrum degenerated upon standing into two ill-resolved signals at ca. 52.3 and 68.9 ppm relative to external TFA; and the HF — $HClO_4$ spectrum exhibited four principal absorptions, at 52.6 (very broad), 63.1, 64.3, and 66.6 ppm, respectively, relative to external TFA. And, the intensity of the signal at 64.3 ppm grew rapidly during scanning of the sample.)

One final set of nmr experiments was performed in an attempt to relate carbenium ion -- carbinol precursor equilibria to associated ^{19}F chemical shift data. The wt % $HClO_4$ datum for 50% ionization of a given carbenium ion species was obtained from the appropriate dilution curve — D.F. plot. A ^{19}F spectrum of a carbenium ion system in this wt % $HClO_4$ was expected to exhibit either two principal signals corresponding to ion and alcohol, respectively, or one signal arising from rapid solution equilibration of ion and alcohol (see p. 101). To carry out this investigation a solution of 4-pyridyl-4-methoxyphenyl-4-fluorophenylmethanol was prepared using 53.8% $HClO_4$. This is the so-called 50% ionizing acid for this carbenium ion precursor. The nmr spectrum of this solution, however, exhibited only a single resonance which corresponded with the position for the ^{19}F signal of this ion in 70% $HClO_4$. Moreover, no additional resonance was detectable for this system until

the acid was diluted to ca. 46%. At this acid concentration a second resonance finally developed which corresponded to the signal exhibited by the protonated pyridylmethanol precursor. These signals became of approximately equal intensity at ca. 44.5% acid, and at ca. 43% acid the carbenium ion resonance disappeared entirely. This result is unusual for the following reasons. First, the dilution curve — D.F. data for this carbenium ion indicate that the carbenium ion — protonated alcohol equilibrium is measurably significant over a minimum range of 8-10% acid (this is, in fact, the case for each of the titratable carbenium ion species, see p. 105), whereas the nmr result suggests that this equilibrium is measurable only over a rather limited range of ca. 3%. Secondly, the nmr result indicates that this particular carbenium ion is essentially 50% reconverted to protonated alcohol precursor at 44-45% $HClO_4$ which is much less than the 53.8% value predicted from the titrimetric investigation. Hence, the nmr measurement suggests that a considerably less concentrated ionizing medium is capable of producing substantial conversion of protonated pyridylmethanol to carbenium ion, and, as yet, this result is unexplainable. It should be noted, however, that there is a significant difference in concentration required for carbenium ion nmr investigations compared to concentrations necessary for carbenium ion electronic spectral investigations. That is, in order to obtain acceptable nmr spectra for materials of relatively high molecular weight which are dilute in the absorbing nucleus (viz., one fluorine atom per pyridylmethanol of M.W. ca. 280-300 amu), it is necessary to maintain solute concentrations at 10^{-2} M, or higher, in order to obtain detectable ^{19}F resonances, even with currently available Fourier transform techniques. In fact, the

4-methoxyphenyl substituted carbenium ion was visually detectable in 43% $HClO_4$ by virtue of the characteristic solution color of the ion, even though no nmr resonance could be obtained. Thus, concentration requirements for nmr studies are considerably greater than for electronic spectral measurements on pyridylcarbenium ions. Hence, the two experimental methods cannot be cross-checked quantitatively owing to the grossly different concentration ranges necessary for each measurement. (Note: The same nmr dilution experiment was performed on the bis complex of 4-pyridyl-4-methoxyphenyl-4-fluorophenylmethanol (carbenium ion). However, this investigation proved futile as dilution induced the precipitation of the complex.)

Although additional studies are required to resolve the problems encountered in the so-called nmr dilution experiments, a potentially fruitful study is suggested concerning the carbenium ions which eject fluorine in $HClO_4 - H_2O$. That is, presume it is possible to fix a known concentration ratio of a given unsubstituted phenylpyridylmethanol and corresponding carbenium ion <u>via</u> appropriate manipulation of $HClO_4$ concentration. This should establish two simultaneous equilibria: a) alcohol interconversion with carbenium ion; and, b) carbenium ion interconversion with the species resulting after fluorine atom loss. This investigation would obviously be monitorable by ^{19}F nmr, and perhaps new information concerning the stability of such types of carbenium ions would be afforded from kinetic, as well as from thermodynamic standpoints.

<u>Linear Free Energy (LFE) Correlations and Carbenium Ion Stability</u>. A number of analytical free energy correlations have been successfully

applied to the thermodynamic data obtained for the pyridylcarbenium ions considered in this work. These correlations are presented graphically (where appropriate) in this section and discussed principally in terms of the relative stabilities of the various carbenium ion species. A significant outgrowth of these considerations is the indication that coordination, which has been shown to stabilize a given carbenium ion relative to the protonated ion, destabilizes the ion relative to the unprotonated, uncoordinated ion (vide infra). This implies, rather obviously, that the localized removal of "sigma" electron density occurring upon coordination to the palladium containing moiety cannot be separated from a concomitant reduction of π-electron density in the pyridine ring. Consequently, it appears that complexation (for the cases considered herein) does in fact destabilize the pyridylcarbenium ions.

Various studies (see, for instance, (12), (19), (77), (78), and (79)) have demonstrated the suitable application of the famous Hammett equation (80), $\log K = \log K^\circ + \rho\sigma$, towards the correlation of thermodynamic parameters for arylcarbenium ions. Therefore it was reasonable to analyze the thermodynamic data obtained for the pyridylcarbenium ions by similar methods.

The plots which are presented in Figures 13, 14, and 15, p. 118, established the following relationships to be linearly dependent:

(i) Hammett "exalted" $\Sigma\sigma_{p^+}$ constants vs. ΔG° of carbenium ion formation. (The σ_{p^+} values employed were 0.00 for para-H; -0.07 for para-F; -0.31 for para-CH_3; and -0.78 for para-OCH_3 (81). Curves 1, 2, and 3, are for protonated 2-pyridyl, protonated 4-pyridyl, and bis-palladium(II) complexed 4-pyridylcarbenium ions respectively.)

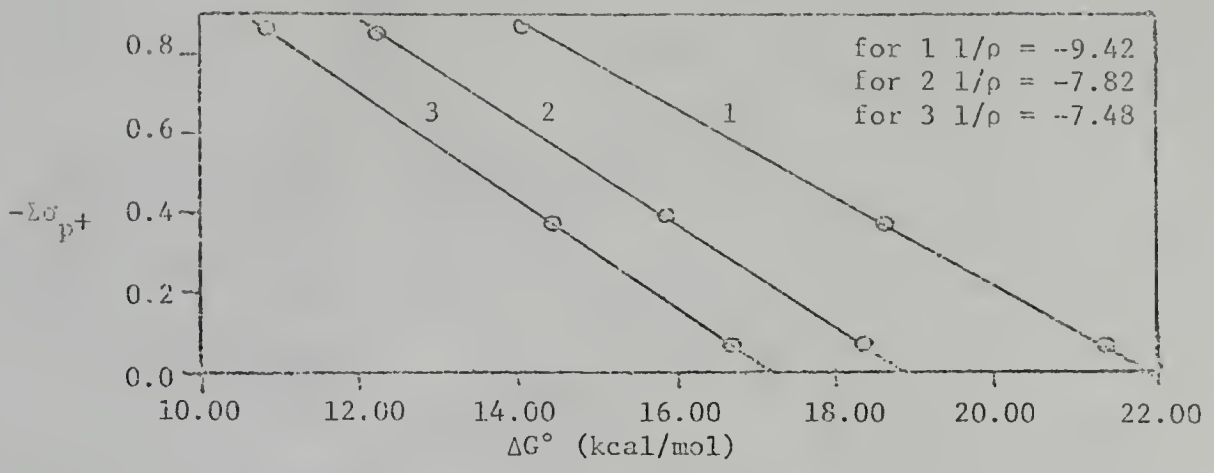


Fig. 13. Hammett $\Sigma\sigma_{p+}$ vs. ΔG°(carbenium ion formation). See p. 117 for explanation

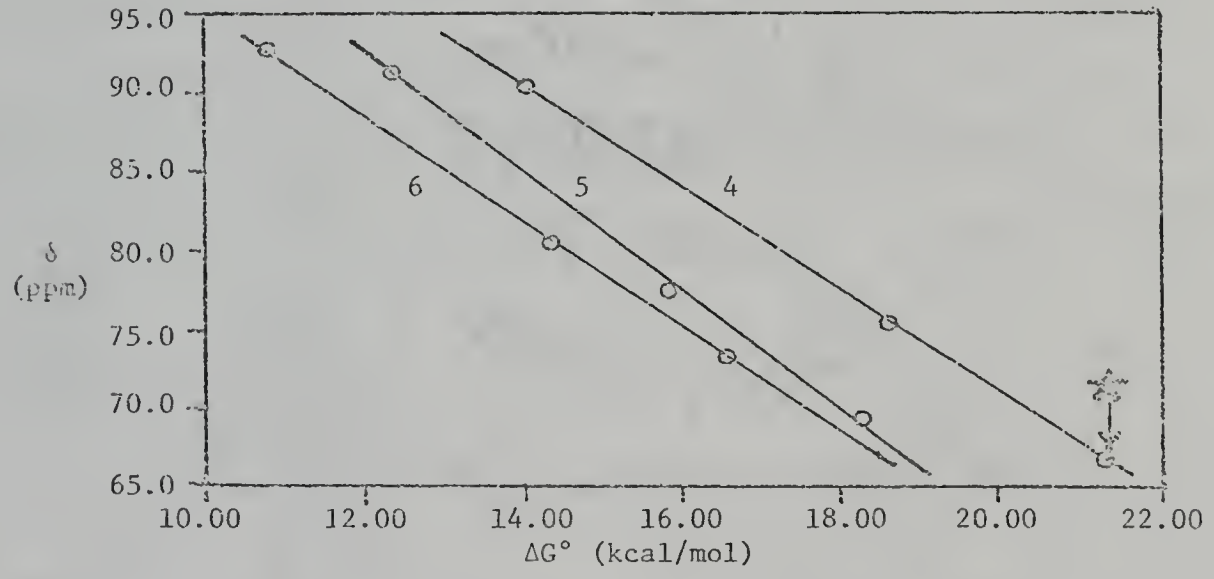


Fig. 14. Carbenium ion δ relative to external $CFCl_3$ vs. ΔG° of same. See p. 117 for explanation.

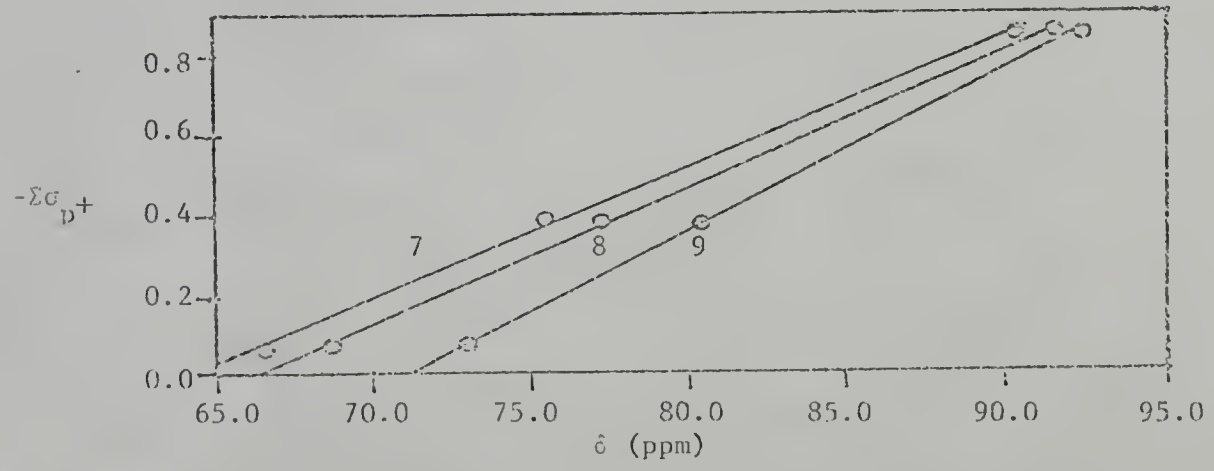


Fig. 15. Hammett $\Sigma\sigma_{p+}$ vs. carbenium ion δ relative to external $CFCl_3$. See p. 117 for explanation.

(ii) Carbenium ion ^{19}F nmr chemical shifts recorded relative to external $CFCl_3$ *vs.* related values of $\Delta G°$. (Curves 4, 5, and 6, correspond to the same carbenium ion sequence as in (i) above. The point on curve 4 designated by the * is extrapolated to the abscissa to yield $\Delta G°$ for the formation of unsubstituted phenyl-2-pyridylcarbenium ion.)

(iii) Hammett "exalted" $\Sigma\sigma_{p+}$ constants *vs.* carbenium ion ^{19}F nmr chemical shifts relative to external $CFCl_3$. (Curves 7, 8, and 9, correspond to the same carbenium ion sequence as in (i) above.) The ensuing discussion is in respect to these relationships. The appropriate application of Hammett σ_{p+} constants (rather than the usual σ constants) in free energy correlation analyses for arylcarbenium ions upon variation of electron donating, *para*-phenyl substituents has been established principally through the work of Deno and Evans (78), and Brown and Okamoto (82). Therefore it was expected that these parameters were found to correlate exceptionally well with the pyridylcarbenium ion stability data. Admittedly, it is seen that in each case the curves have been drawn employing only three data points. None the less, the degree of linearity obtained for all correlations considered is astonishingly good. And, although in certain instances nonlinear free energy correlations may prove to be interesting and important, a linear correlation is the required *sine qua non* for the immediate and direct prediction of interrelated but otherwise "unknown" thermodynamic information. Indeed, it is on this basis that the stability constant data reported for 2-pyridylphenyl-4-fluorophenylcarbenium ion (Table V, pp. 95-96) have been obtained and deemed reliable. That is, plots 2 and 3 in Figure 13 served to establish the linear interdependency of $\Sigma\sigma_{p+}$ and $\Delta G°$ for carbenium ion formation for the various 4-pyridyl species.

Similarly, plots 7, 8, and 9, have demonstrated the linear relationship of $\Sigma\sigma_{p^+}$ and δ for each carbenium ion species investigated. Hence, as shown, the construction of plot 4 in Figure 14 using the nmr and ΔG° data for the 2-pyridyl-4-methylphenyl, and 2-pyridyl-4-methoxyphenyl protonated carbenium ions, allowed the determination of ΔG° for the corresponding unsubstituted phenyl ion. (Note: For these analyses the nmr data recorded relative to external $CFCl_3$ were used exclusively owing to the greater significant figure accuracy obtained for carbenium ion chemical shifts measured relative to this standard. Viz., as indicated by the data contained in Table VI, pp. 110-111, the positions of the sample and reference signals with external TFA as standard were relatively close. Consequently, only two significant figure reliability could be obtained for the nmr data measured relative to external TFA. Nevertheless, to check these LFE analyses, similar plots were drawn using the TFA referenced nmr data, and these plots also were linear.)

Two additional LFE plots of interest are illustrated in Figures 16 and 17, p. 121. The linearity of these plots suggests a proportionate change in carbenium ion stability throughout the related 4-pyridyl vs. 2-pyridyl (Figure 16), and 4-pyridyl vs. bis-complexed 4-pyridyl (Figure 17), series of ions. The slope (= 0.829) of the line in Figure 16 reflects the lower stability of a given 2-pyridylcarbenium ion compared to its 4-pyridyl congener. Extrapolation of this curve to the intercept, however, yields an inexplicable result from which it is implied that for relatively stable pyridylcarbenium ions (i.e., ΔG° very small, or negative) the 2-pyridyl ions are ultimately the more stable. Consequently, it appears that extrapolation of this curve to a considerable extent beyond the data points is not warranted. The slope (= 1.04) of Figure 17

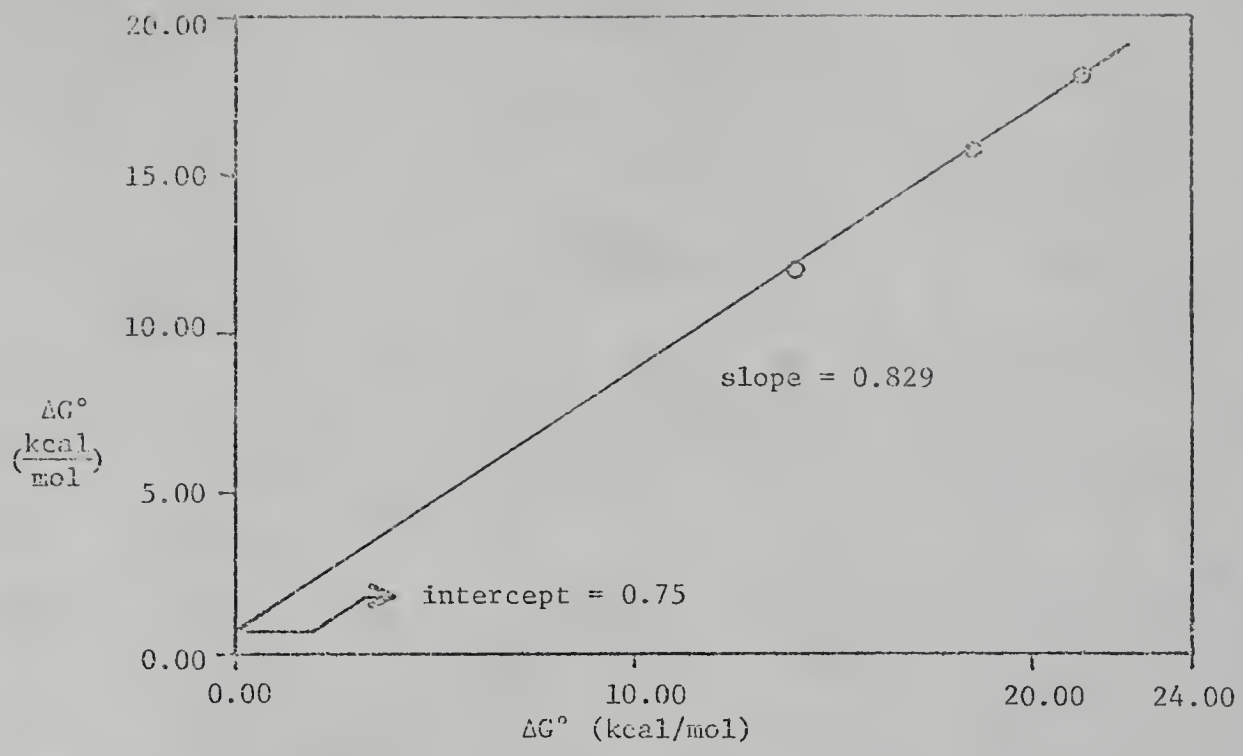


Fig. 16. ΔG°(uncoordinated 4-pyridylcarbenium ions) vs. ΔG°(uncoordinated 2-pyridylcarbenium ions).

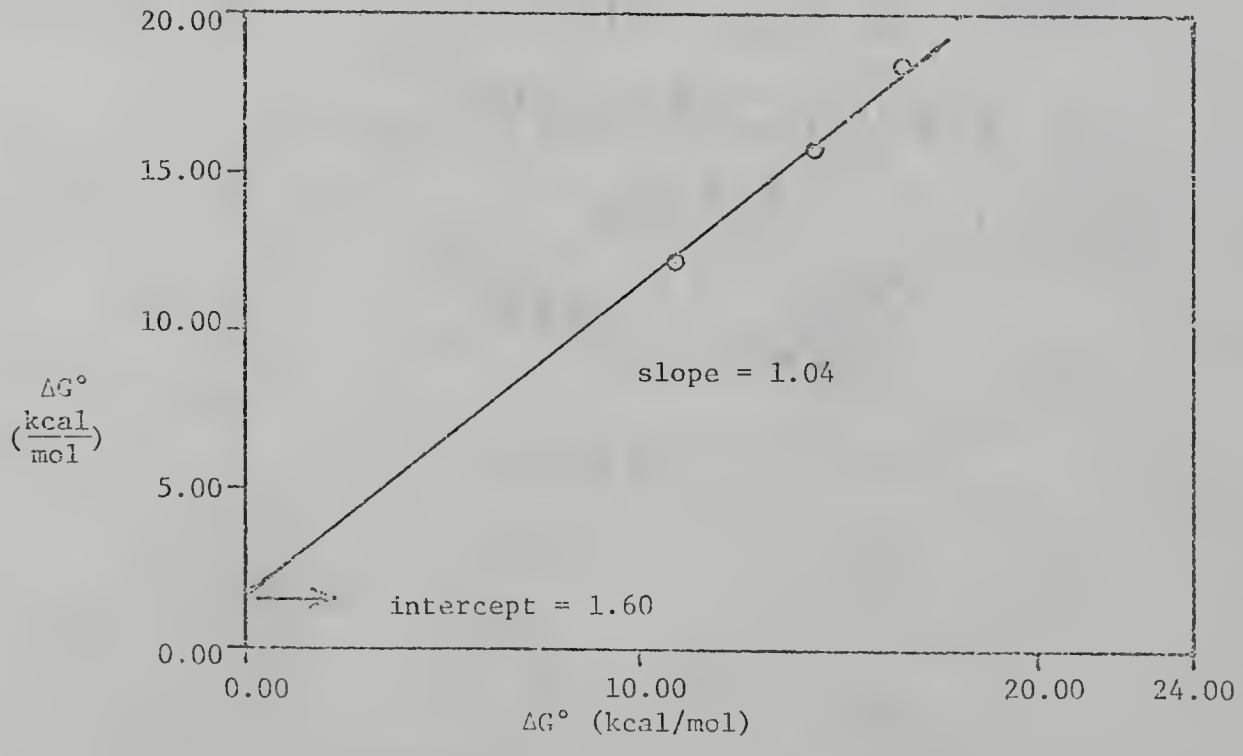


Fig. 17. ΔG°(uncoordinated 4-pyridylcarbenium ions) vs. ΔG°(bis-complexed 4-pyridylcarbenium ions).

corroborates the conclusion previously arrived upon that complexation stabilizes the least stable 4-pyridylcarbenium ion to the greatest extent. In this case the intercept value implies that a coordinated pyridylcarbenium ion is inherently more stable than the corresponding protonated ion. This is a reasonable result. Of course, identical analyses of new, related data are required before more exacting conclusions can be drawn. (Note: Several other linear plots are constructible using the accumulated thermodynamic data owing to the established linear interdependencies (as shown) of $\Delta G°$, σ_{p+}, and δ. These plots can be synthesized as necessary for supplementary correlation studies.)

An examination of the slopes of the curves of Figures 13, 14, and 15 ($1/\rho = -9.42$ for curve 1; $1/\rho = -7.82$ for curve 2; and $1/\rho = -7.48$ for curve 3; these slopes are reported as $1/\rho$ for the comparisons which are to be made) affords a simple method for comparing the stabilities of the pyridylcarbenium ions to related systems of arylcarbenium ions which have been investigated previously *via* similar techniques. That is, as pointed out by Freedman (64:1548), a plot of $\Delta G°$ *vs.* $\Sigma\sigma_{p+}$ for a series of structurally and substitutionally related arylcarbenium ions yields a straight line whose slope reflects the degree of electronic demand at the carbenium ion center. And, in these cases, a negative slope indicates that the presence of electron releasing substituents capable of interacting conjugationally with the carbenium ion positive charge facilitates the development of that charge. Thus, carbenium ion stability is enhanced by substituents such as *para*-methyl and *para*-methoxy relative to *para*-H, etc. Also, the magnitude of the slope is a relative measure of the stability of the particular family of ions under consideration. For example, ρ for plots of ΔG_{R+} *vs.* $\Sigma\sigma_{p+}$ is on

the order of -2.5 for a series of malachite green carbenium ions, -4.5 for a series of tritylcarbenium ions (64:1749), and -8 for para-substituted diphenylmethylcarbenium ions (64:1550). Therefore the stabilities of the pyridylcarbenium ions are again shown to be in the order: Coordinated 4-pyridyl > protonated 4-pyridyl > protonated 2-pyridyl; and furthermore, these results imply that the 4-pyridyl ions are but minimally more stable than diphenylmethylcarbenium ions, whereas the 2-pyridyl ions are appreciably less stable.

Finally, the use of certain, appropriate arguments permit a reasonable comparison of the stability of the protonated and complexed 4-pyridylcarbenium ions to the stability of such ions premised upon a non-bound pyridine nitrogen. That is, although it is not possible, obviously, to investigate an unprotonated free ligand pyridylcarbenium ion in strongly acidic media, it is necessary to speculate on the stability of this ion in order to estimate the net stabilizing effect exerted by the metal containing moiety on the coordinated ion. This is done in the following fashion. The contribution to the stability of a triaryl-type carbenium ion by an unprotonated pyridine ring may be approximated using the literature pK_{R+} values for malachite green (MG) carbenium ion (pK_{R+} = 7.07) and 4-pyridine malachite green (4-pyMG) carbenium ion (pK_{R+} = 5.66). These data have been taken from the compilation of Nemcova et al. (83). (Note: Here pK_{R+} corresponds to the equilibrium reconversion of carbenium ion to precursor alcohol: $R^+ + 2\ H_2O \rightleftarrows R\text{-}OH + H_3O^+$; and 4-pyMG is simply MG with the unsubstituted phenyl ring replaced with a 4-pyridyl ring.) An examination of these pK_{R+} values indicates that exchange of a phenyl ring for a 4-pyridyl ring induces a net carbenium ion destabilization of 1.41 pK units (1.92 kcal) in

the MG series of ions. This destabilization may be quantitatively related to strictly triphenyl-type carbenium ions (i.e., those without para-amino substituents) by comparing the slopes (ρ's) of the plots of log K vs. $\Sigma\sigma_{p^+}$ for the MG series of ions (ρ = -1.4) to that for the triphenyl ions (ρ = -3.5), (84:101-102). That is, as pointed out by Bine, phenyl ring substitution in the triphenyl ions induces a considerably greater change in carbenium ion stability than does the identical substitution in the MG series of ions. Hence, the larger negative slope of this plot for the triphenyl ions reflects the greater sensitivity of the stability of these ions to electronic effects. This consideration is illustrated through a simple analysis of the pK data given below. These data are in respect to the general equilibrium described above.

(i) pK_{R^+} of triphenylcarbenium ion = -6.63; and pK_{R^+} of para-nitrotriphenylcarbenium ion = -9.15 (10).

(ii) pK_{R^+} of MG carbenium ion = 7.07; and pK_{R^+} of para-nitroMG carbenium ion = 6.00 (64:1534). Thus, as expected, the destabilizing effect exerted by a para-nitro substituent is much greater in the triphenyl series of carbenium ions (-2.52 pK units) than in the MG series of carbenium ions (-1.07 pK units). And, the ratio of these destabilizing contributions, 2.52/1.07 = 2.36, is certainly comparable to that predicted from the slope ratio, 3.5/1.4 = 2.5. Now, in that pyridine exhibits tendencies towards electrophilic aromatic substitution which are similar to nitrophenyl rings, and since both of these systems destabilize trityl-type carbenium ions, it is reasonable to predict pK_{R^+} for unprotonated 4-pyridyldiphenylcarbenium ion to be on the order of -6.82 - 2.5(1.41) = -10.34 = pK_{R^+}. (Note: For this approximation -6.82 is the value for pK_{R^+} of triphenylcarbenium ion. This is the average of

the pK_{R+} values cited in Table V, pp. 95-96, for this ionic species in 70% $HClO_4$.) A comparison of this value (-10.34) to the pK_{R+} values which have been determined for the protonated (pK_{R+} = -13.47) and bis-complexed (pK_{R+} = 12.21) 4-pyridylphenyl-4-fluorophenylcarbenium ion, strongly suggests that the unprotonated ion is appreciably more stable than either the protonated (obviously) or the palladium complexed ion. Moreover, the para-fluoro substituent would contribute additional stabilization to this ion such that the actual pK_{R+} would be slightly greater (less negative) than the speculative value of -10.34. This further substantiates the validity of the hypothetical stability comparison.

Suitable use of the log K vs. $\Sigma\sigma_{p+}$ plots given by Hine (84:101) in conjunction with the results of Barker et al. (52) affords another simple corroboration of this consideration. That is, examination of the plot for the MG series of ions (Hine) reveals that for MG with pK_{R+} = 7.07, $\Sigma\sigma_{p+}$ = -3.4; and for 4-pyMG with pK_{R+} = 5.66, $\Sigma\sigma_{p+}$ = -2.5. Thus, with σ_{p+} = -1.7 for para-$N(CH_3)_2$, a hypothetical value of σ = 0.9 is predicted for a 4-pyridyl ring, thereby demonstrating the electron withdrawing capacity of a pyridine ring taken as an arylcarbenium ion substituent. This value is comparable to σ_p = 0.78 for a nitro group as a para-phenyl substituent; and the ratio 0.9/0.78 = 1.2 is in good agreement with the ratio 1.41/1.07 = 1.3 which is obtained from the respective energetic destabilizations of a 4-pyridyl ring and a 4-nitrophenyl ring in MG carbenium ion. Similarly, the linear correlation of $\bar{\nu}_{max}$ (kK) with Hammett σ substituent constants discovered by Barker and coworkers for a series of phenyl substituted MG carbenium ions

allows a prediction of σ of ca. 1.0 – 1.1 for the 4-pyridyl ring in 4-pyMG. This correlation is made by using the value of 15.4 kK reported for $\bar{\nu}$ at λ_{max} for 4-pyMG (83). Furthermore, use of the second linear plot presented by Hine of log K vs. $\Sigma\sigma_{p+}$ for triphenylcarbenium ions, and the provisional value of ca. -10.3 for pK_{R+} of unprotonated 4-pyridylphenylcarbenium ion, allows a value of σ of ca. 1 to be obtained for the 4-pyridyl ring. Thus, the hypothetical σ values which are predicted for a 4-pyridyl ring treated as a substituent in arylcarbenium ions are found to be in very good agreement. Therefore, on this basis, it is reasonable to conclude that an unprotonated pyridine ring is of approximately the same electron withdrawing capacity as a nitrophenyl ring, but, as suggested previously, is not as electron withdrawing as the palladium complexed pyridine ring.

A last extension of these considerations can be made employing the results of Atkinson et al. (85). These workers satisfactorily demonstrated the existence of a linear correlation between the frequencies ($\bar{\nu}$, kK) of the longest wavelength electronic absorptions and Taft σ* polar substituent constants for a family of diphenylmethylcarbenium ions ($\phi_2\overset{+}{C}$-X) generated in 96% H_2SO_4. The group X is the substituent which is varied in this series of ions. Here, σ* reflects the electron releasing or withdrawing capacity of X depending upon the exertion of polar effects by X. Since the 4-pyridylcarbenium ions are of comparable stability to the diphenyl ions (p. 122) and have exhibited about the same sensitivity to changes in electronic environment at the carbenium ion center as these ions (recall the similar ρ values for plots of ΔG° vs. $\Sigma\sigma_{p+}$ for these ions), it is reasonable to estimate values of σ* for the protonated and coordinated pyridine rings taken as polar substituents.

In fact, this treatment may indeed be more logical than the σ evaluation owing to the polar character produced in the pyridine ring by protonation (and, apparently, by coordination as well). Inasmuch as the electronic spectral investigations have indicated that the absorption at λ_{max} reflects principally electronic interactions between the carbenium ion center and the phenyl rings, it is necessary to consider the frequencies at λ_{max} for the protonated and bis-palladium complexed unsubstituted 4-pyridyldiphenylcarbenium ion. The frequencies are 21.0 kK and 21.4 kK, respectively, for these ions in 96% H_2SO_4 (7). (Note: The electronic spectra of these ions are not changed in 70% $HClO_4$.) Using the $\bar{\nu}$ — σ* correlation plot (85) hypothetical values of σ* of ca. 1.0 for protonated pyridine, and σ* of ca. 0.85 for palladium-complexed pyridine are obtained. These σ* values indicate rather substantial electron withdrawing capacities for these pyridine moieties. Again, based upon the comparable stabilities expected for 4-nitrotriphenylcarbenium ion and unprotonated 4-pyridyldiphenylmethylcarbenium ion, a speculative value of σ* can be estimated for the unprotonated pyridyl ring. That is, since $\bar{\nu}$ at λ_{max} for the nitro ion is 22.0 kK, which correlates with σ* of ca. 0.6, a value of σ* of ca. 0.6 — 0.7 is predicted for the unprotonated pyridyl ring. Of course, this speculation rests on the assumption that these two ring systems influence the frequency at λ_{max} to approximately equal extents. This contention is supported by the fact that these ring systems have been shown to be of comparable electron withdrawing capacity. Therefore, as indicated previously, the palladium(II) containing moiety employed in this work as the coordinating agent, appears to contribute an overall thermodynamic destabilization to trityl-type pyridylcarbenium ions.

IN CONCLUSION

The experimental bases which have been established for the investigation of heteroaromatic carbenium ions (6, 7, and 8), have been reinforced and expanded by this work. The achievements which are felt to be of principal significance are the following:

(i) The preparation of the mixed "mono" alcohol complexes (denoted in the text as $[Pd(II)(pyLOH)(L_N)Cl_2]$) appears to be the first successful application of a synthetic method generally suitable for the selective incorporation of strong π-acid ligands into the coordination sphere of palladium(II), to include pyridine-type donors. Consequently, it is now expected that pyridine containing arylcarbenium ion precursors can be introduced as ligands ad libitum into palladium(II), as well as certain other, metal centers. Therefore, many additional, related studies on complexed carbenium ions have been made feasible by the development of this synthetic technique.

(ii) The thermodynamic stabilities determined for the various carbenium ion species considered herein provide strong evidence to indicate that charge repulsion effects tend to destabilize the 2-pyridyl ions to a considerable degree. On the other hand, the very similar stabilities found for related "mono" and "bis" complexed carbenium ions indicate that charge repulsion effects in the doubly ionized "bis" ion systems are no longer sufficient to destabilize these ions. So, it is

potentially of value to prepare several "bis" carbenium ion complexes with the interesting prospect of determining the sensitivity of the stability of a particular complexed carbenium ion to intra-species charge repulsion effects. Moreover, carbenium ion stabilization provided by various metal-containing coordination centers can be considered in respect to this possibility. That is, effects on carbenium ion stability resulting from variation of the central metal species, variation of the oxidation state of the metal species, variation of the counter ligands, etc., can now be investigated with similar intent.

(iii) Again, the results obtained from the "Deno" titration stability measurements, established to be reliable by appropriate LFE analyses, have shown that this titrimetric technique is a suitable method by which to evaluate the thermodynamic stabilities of protonated and complexed pyridylcarbenium ions. Furthermore, successful electronic spectral interpretations have provided experimental and theoretical substance towards correlating arylcarbenium ion electronic absorptions with the aromatic ring systems which comprise the carbenium ion entity. Consequently, it has been made possible to assess tentatively the contribution to coordinated carbenium ion stability exerted by various metal containing moieties in terms of the relative degree of influence upon the frequency of the so-called y-band electronic absorption as measured for the different metal centers.

(iv) The applicability of ^{19}F nmr chemical shift measurements as a criterion of the stability of pyridylcarbenium ions has been established. That is to say, a fluorine nucleus <u>para</u> substituted on a phenyl ring has been shown to be a suitably sensitive probe for the purpose of quantitatively estimating the stabilities of these types of carbenium

ions. A possibly fruitful extension of this work might well be provided by ^{19}F nmr measurements with the fluorine nucleus incorporated as a meta phenyl substituent in the carbenium ion molecular framework. By a comparison of the results of these nmr investigations with the nmr data at hand, a separation of σ- vs. π-electronic effects within the pyridylcarbenium ions is potentially achievable.

(v) The LFE correlations which have been applied to the thermodynamic stability data, ^{19}F nmr data, and the appropriate Hammett-type substituent constants, have proved to be exceedingly good even though only three data points were used for each analysis. Obviously, the preparation and investigation of additional pyridylcarbenium ion species by varying para phenyl ring substituents, affords a simple means of extension of the current work. The stability predictions made in reference to unprotonated 4-pyridyldiphenylcarbenium ion could be pursued experimentally via the syntheses of salts of the various pyridylcarbenium ions, followed, of course, by appropriate measurements to determine the stability of these ions. The preparation of stable salts of the coordinated carbenium ions could well be stimulating and provocative owing to the stringently anhydrous, nonbasic, conditions required in order to sustain the existence of such materials. Consequently, it could prove difficult to develop a preparative route during which the metal containing moiety would remain coordinated during the conversion of alcohol to carbenium ion salt.

To recapitulate then, the experimental studies on the various carbenium ion species which have been carried out during this work have been very successful. It is therefore proposed that the scope of thermodynamic investigations upon free and complexed heteroaromatic

carbenium ions can now be broadened considerably by extending these studies to include related systems of arylcarbenium ions.

APPENDIX

1. Specific Gravity of Aqueous $HClO_4$ Determined as a Function of Wt % $HClO_4$. By employing the specific gravity (ρ) — wt % $HClO_4$ data in Table IV, p. 91, a computer fitted "least squares" estimate of ρ as a function of wt % $HClO_4$ was obtained. This was carried out by assuming the functional relation $y(\rho) = f(x)$ (x = wt %) to be of the form:

$$y = a_o + a_1x + a_2x^2 + a_3x^3 + a_4x^4 \qquad \{15\}$$

for y vs. x which yields a smooth curve plot over the entire range of experimental (x,y) values. Then, the values of the coefficients (a's) for this polynomial are obtained from a least squares estimates analysis by minimizing the sum of the squares of the deviations which result from:

$$(\text{deviation})^2 = [y(\text{calcd from } \{15\}) - y(\text{exptl})]^2 \qquad \{16\}$$

summed over all the experimental points. With the a's calculated, equation {15} is:

$$y = 0.996357669170\text{ex }00 + (0.606617134345\text{ex} - 02)x - (0.171560538090\text{ex} - 04)x^2 + (0.164401851371\text{ex} - 05)x^3 - (0.981691970813\text{ex} - 08)x^4 \qquad \{17\}$$

from which a complete series of ρ values as a function of wt % $HClO_4$ is obtained. (Note: it was found that the x^3 and x^4 terms may be neglected with no loss in data precision to 4 significant figures.) These data were processed at intervals of 0.010 wt % spanning the range

ρ = 0.996357 at wt % $HClO_4$ = 0.000 (i.e., pure water at 25°), to ρ = 1.737627 at wt % $HClO_4$ = 75.000. The ρ values were rounded to 4 significant figures for the required D.F. calculations. The program employed was: WANG Series 700 V 1. General Library, Program 1063A/ST3 – "N^{th} order regression analysis". A general description of the method is provided by Kuo (86).

2. Degree of Protonation of a Pyridylmethanol (pyLOH) in Aqueous $HClO_4$. In reference to the assumption that a pyridylmethanol is of approximately the same basicity as pyridine (p. 99), straightforward acid-base equilibrium calculations may be employed showing that the degree of pyridine ring protonation is virtually 100%:

(i) In connection with this assumption the following equilibria can be written:

$$pyLOH + H_2O \rightleftarrows H^+pyLOH + OH^- \qquad \{18\}$$

and

$$H^+pyLOH + H_2O \rightleftarrows pyLOH + H_3O^+ \qquad \{19\}$$

(ii) Using {19} and $K_b = 2.3 \times 10^{-9}$ for pyridine, the equilibrium constant for {19} can be evaluated:

$$K_{\{19\}} = \frac{[pyLOH][H_3O^+]}{[H^+pyLOH]} \times \frac{[OH^-]}{[OH^-]} = \frac{K_w}{K_b}$$

and

$$\frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{2.3 \times 10^{-9}} \simeq 4.3 \times 10^{-6}$$

(iii) Now, with the conditions specified as $[H_3O^+] = 1$ and $[pyLOH]_{init.} = 0.01$ (p. 99), it follows that for

$$pyLOH + H_3O^+ \rightleftarrows H^+pyLOH + H_2O \qquad \{20\}$$

$$K_{\{20\}} = \frac{1}{K_{\{19\}}} = \frac{1}{4.3 \times 10^{-6}} = 2.3 \times 10^5$$

and, if $[H^+pyLOH] = x$,

$$K_{\{20\}} = \frac{[H^+pyLOH]}{[pyLOH][H_3O^+]} = \frac{x}{(0.01 - x)(1 - x)} = 2.3 \times 10^5$$

and

$$\frac{x}{(0.01 - x)(1 - x)} \simeq \frac{x}{0.01 - x} \quad \text{since } 1 >> 0.01 > x$$

and for

$$\frac{x}{0.01 - x} \simeq 10^5 = \frac{10^{-2}}{10^{-7}}$$

x is on the order of ca. 0.0099999! Hence, within the limits of the calculation, a given pyridylmethanol at ca. 0.01 M (initially) is protonated to an extent of 100% in 1 M $[H_3O^+]$.

3. Experiments Conducted upon the Carbenium Ion Species Found to Exhibit Rearrangement in 70% $HClO_4$. As indicated by previous investigations which have employed acidic media to generate arylcarbenium ions containing para-fluorophenyl substituents, the fluorine atom may eventually be displaced resulting in the formation of either an alcohol (68) or a quinone (79). Consequently, loss of the para-fluorine substituent from the pyridylphenyl-4-fluorophenylcarbenium ions in the $HClO_4 - H_2O$ was not unusual since in these carbenium ion systems the para-fluoro substituent is the predominant electron-donating entity involved in conjugational interaction with the carbenium ion center. Therefore positive charge build-up at the para-position in the fluorine-containing ring ultimately results in nucleophilic displacement (presumably by H_2O solvent molecules) of the fluorine substituent.

In recording the electronic spectra of these pyridylphenyl-4-fluorophenylcarbenium ion species it was observed that the intensity of the main absorption bands (the x and y bands) grew steadily upon standing until the intensities had approximately doubled. Moreover, it was observed that the positions of these bands remained essentially unchanged during rearrangement of the uncoordinated ions, whereas the mono-complexed $[Pd(II)(L_N)Cl_2pyL]^+$ carbenium ion exhibited an x-band shift to 494 nm after standing a period of 12 days. (Recall that λ_{max} for this carbenium ion as the protonated species is 482 nm, and λ_{max} for this particular complexed ion is 477 nm). Thus, it is seen that the "new" λ_{max} (494 nm) is appreciably longer even than λ_{max} for the free (protonated) ion (482 nm). Also, the bis-complex of this ion exhibited a shift in λ_{max} from 470 nm to 482 nm after standing a period

of 6 days; this species, however, exhibited no further red shift of the x-band absorption as did the corresponding mono-complexed ion (above). These results are as yet not explicable.

In an attempt to estimate the relative stability of the rearranged product, assuming it to be a new arylcarbenium ion, this species was titrated *via* the usual method. This was carried out by preparing a fresh sample of 4-pyridylphenyl-4-fluorophenylcarbenium ion in 70% $HClO_4$ and titrating immediately. The sample was then allowed to stand *ca.* 24 hours during which time the intensity of the x-band absorption had essentially doubled. This result indicated that although the original carbenium ion had been substantially reconverted to protonated alcohol precursor by titration, the protonated precursor was still capable of rearranging to the new species thereby implying that the new species was a more stable carbenium ion. After the intensity of the x-band had become constant, indicating that rearrangement was complete (under these conditions), the titration was repeated. This second titration required approximately three times as much titrant (water) in order to effect the same absorption fall-off as compared to the initial titration. So, again, this species appeared to be a more stable carbenium ion than the original pyridylphenyl-4-fluorophenyl ion from which it was derived.

Finally, a sample of 4-pyridylphenyl-4-fluorophenylmethanol (*ca.* 100 mg) was dissolved in 70% $HClO_4$ (*ca.* 10 ml of acid) to completely convert it to carbenium ion. Rearrangement was again monitored spectroscopically, and after it was apparent that no further changes in the electronic spectrum of the sample were occurring, the acid was neutralized by the careful addition of reagent NH_3. This resulted in the

separation of a mixture of a white crystalline solid and a rather gummy yellow solid. The mixture of solids was transferred to a filter and washed with copious quantities of deionized water. The white solid was readily removed by the washing, and the yellowish material remained on the filter. The contents on the filter were air dried to yield ca. 15 mg of a yellow-orange amorphous solid. This material exhibited decomposition to a brown-black oil above 140° and an IR analysis revealed that this material was different than the original alcohol. A visible spectrum of this material in 70% $HClO_4$ was identical to that previously obtained for the so-called rearrangement product. The ^{19}F nmr spectrum of this material in 70% $HClO_4$ was also recorded. Following 3000 scans with the Fourier transform synthesizer two weak signals (at 37.7 ppm and 68.9 ppm upfield with respect to external TFA) were detected. These signals did not correspond to any of the nmr signals which had been recorded relative to external TFA during previous carbenium ion nmr analyses; and the very low intensities of these signals indicated the absence of any appreciable concentration of fluorine in the sample. Mass spectral cracking analyses of this material revealed the presence of molecular ion fragments of nominal mass as high as 520.5 amu; and, at relatively low probe temperatures (200° or less) a 259 amu base peak was consistently observed. Interestingly, the 259 peak corresponds to the mass of the quinone species which would result from the combined effects in the parent alcohol, of quinone formation at the original fluorine site and hydroxyl loss at the exocyclic carbon. Careful analyses of these spectra, however, suggested the presence of as many as four new compounds with the distinct possibility of one or more of these materials existing as a polymer. Rather obviously

therefore, the nature of the material(s) produced upon fluorine atom displacement from the pyridylphenyl-4-fluorophenylcarbenium ions in $HClO_4 - H_2O$ remains to be ascertained.

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BIOGRAPHICAL SKETCH

James Charles Horvath was born June 29, 1942, in Toledo, Ohio. He was very fortunate to recognize that learning is a wonderful experience which life forever offers. Who knows what may lie ahead?

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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